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The Degradation of Methyl β-D-Glucopyranoside by Oxygen in Alkaline Solution

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THE DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE BY OXYGEN IN ALKALINE SOLUTION

A thesis submitted by

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SUMMARY

The bleaching of cellulosic pulps with oxygen and alkali (oxygen bleaching) is becoming an increasingly attractive process for the pulp and paper industry, especially regarding its greatly reduced stream pollution load. However, unless a "protector," such as magnesium carbonate, is present during bleaching, the pulps undergo considerable degradation that is characteristic of chain scission.

In the present investigation, methyl β-D-glucopyranoside (MBG) was employed as a cellulose model to increase the understanding of the chain scission reaction and the factors that affect it. Reactions were run in tube-type reactors lined with teflon to prevent interference by metals. Reactions were faster in stainless steel reactors.

The initial rate of reaction of MBG at 120°C. was found to be second-order in glucoside and first-order in both oxygen (34.5-74.5 p.s.i.) and sodium hydroxide (0.5-1.25N), with an apparent activation energy of 21 kcal./mole between 100 and 120°C. The sodium hydroxide dependence was slightly curvilinear; increasing with concentration. The nonlinearity might be due to inadvertent variations in oxygen concentration caused by uncertainties in the relationship between oxygen pressure, dissolved oxygen, and alkali concentration. Other possible causes include salt effects and multiple reaction pathways having different alkali dependencies.

Peroxides were formed during the reaction, but neither induction periods nor autocatalysis were observed.

Derivatives of MBG having blocked, or missing, hydroxyl groups were used to study the influence of hydroxyl groups of the molecule on reactivity. Methyl tetra-O-methyl β-D-glucoside was unreactive, suggesting that hydroxyls are needed for reaction. Methyl β-D-xyloside and methyl 6-deoxy β-D-glucoside

were only slightly less reactive than MBG, indicating that the C6 hydroxyl has little influence on the reaction rate. Methyl 3,4,6-tri-O-methyl β-D-glucoside, having only the C2 hydroxyl unblocked, reacted much more slowly than MBG, but methyl 2-deoxy β-D-glucoside reacted slightly faster than MBG. Methyl 3-O-methyl (α,β)-D-glucoside was less than half as reactive as MBG. Thus, it is concluded that no particular hydroxyl group can sufficiently account for the reactivity of MBG.

Hydroquinone and glucose increased the initial rate of degradation of MBG, probably because they are oxidized and produce peroxides that, in turn, attack the glucoside.

Magnesium carbonate inhibited the reaction, but the effect was small compared to that anticipated from its influence on cellulose degradation during oxygen bleaching.

Methanol liberation from MBG accompanied glucoside degradation under all conditions, but only about one-half mole of methanol was produced for each mole of glucoside reacted. All the methanol could be recovered upon subjecting the reaction solutions to acid hydrolysis. Therefore, it is evident that the degradation of MBG does not always lead immediately to glucosidic bond cleavage and involves, at least in part, the formation of a product with the aglucone still attached.

D-Methoxy-D'-hydroxymethyl diglycolic acid, the isomer of the possible C2,C4 dicarboxylic acid product of MBG, reacted more slowly than MBG by a factor of more than ten. Hence, oxidative cleavage of carbon-carbon bonds could yield a product of sufficient stability to account for the "bound" methanol.

At least two acidic products were detected in low concentrations by gas-liquid chromatography; one was tentatively identified as arabinonic acid. None was detected when products of stainless steel corrosion were present during reaction.

It is postulated that methyl β-D-glucoside reacts with oxygen in alkaline solution through a complex mechanism involving ionization of a hydroxyl function, followed by direct oxidation of the group with oxygen. Subsequent reactions result in glucosidic bond cleavage or formation of a product containing "bound" methanol.

The degradative enhancing effects of hydroquinone and glucose and the recognition that analogous materials are present in unbleached pulps suggest that peroxides formed in their oxidations may attack cellulose and thereby contribute greatly to the overall rate of degradation of cellulose during oxygen bleaching. Since magnesium ions complex with peroxides, the protective influence of magnesium carbonate may arise from the reduction of competing reactions by deactivation of peroxides through complex formation.

In addition, to simplify future model studies a design is proposed for a teflon-lined reactor that can be sampled during operation.

INTRODUCTION

OXYGEN BLEACHING

The use of oxygen and alkali for delignifying and brightening cellulosic pulps is currently attracting much attention. Although the basic idea was first considered at least thirty years ago (1), the development of an industrial process is just now being achieved. The most significant technological contributions have been made in the last fifteen years.

Nikitin and Akim (2-3) clearly demonstrated the bleaching action of oxygen and alkali on wood pulps, but found that the mechanical properties of the pulps deteriorated during bleaching. Then Robert, et al., (4-6) discovered that some alkaline earth carbonates, notably magnesium carbonate, could be used to protect the strength characteristics of the pulp. This discovery made possible the development of a commercially feasible process now called oxygen bleaching (7).

Oxygen bleaching is basically a simple process in which the unbleached pulp at ca. 20% consistency is treated with sodium hydroxide (8-12%, based on pulp) and oxygen (up to 15 bars) at temperatures of 90 to 130°C. Magnesium carbonate is added to minimize the degradation of the cellulose. The main advantage of oxygen bleaching is that it can greatly reduce the stream pollution normally associated with the C-E-H stages of traditional bleaching processes (7).

Recently, oxygen bleaching has been applied with moderate success to high-yield pulps (8-10) and nonwoody cellulosic materials (11-12). Thus, the potential of oxygen bleaching is evident. However, since the cellulose is

oxidized, as well as the lignin, the broad application of the process will depend largely on the ability to control the degradation of the cellulose. This demands a much better understanding of the mechanism by which "protectors," such as magnesium carbonate, inhibit the degradation.

The presently available information about the degradation reactions is insufficient to permit the formulation of reasonable hypotheses regarding the protective role of magnesium carbonate. Consequently, this author felt that a study of the degradative reactions themselves would be more informative at this stage.

LITERATURE REVIEW

OXIDATION OF CELLULOSE DURING OXYGEN BLEACHING

During oxygen bleaching in the absence of a "protector," cellulosic pulps undergo a large reduction in their physical strength properties. The degree of polymerization (D.P.) is lowered considerably, but yield losses are moderately low (4). These phenomena suggest that degradation occurs mainly through scission of the cellulose chains, or depolymerization, rather than through endwise "peeling" of fragments from the cellulose molecule, but the reactions have received little investigation.

Studies with Cellulose

Golova and others (13-17) carried out a series of investigations of the degradation of cellulose under conditions similar to those used in oxygen bleaching, except that air was bubbled through the suspensions. Studies with purified cotton and regenerated cellulose showed that the degradation was greatest in the accessible regions of the cellulose (14-15). Cellulose with a

high proportion of ordered regions reacted at a sharply reduced rate without a change in D.P. (14).

The carbonyl content of the cellulose was found to influence the rate of degradation; higher carbonyl content led to faster rates (13-16).

Peroxides were detected, and their concentrations were directly proportional to the rate of degradation of the cellulose preparation (14). The concentration of peroxides formed on oxidation of regenerated cellulose possessing a relatively large content of disordered regions exceeded twice that found on oxidation of native cellulose. Peroxides were formed when the carbonyl content was reduced. Thus, it was concluded that peroxides originated not only from the carbonyl groups, but also from the hydroxyl groups (14). Furthermore, the formation of peroxides in the oxidation of cellulose preparations containing "minimum contents" of carbonyl groups was interpreted as confirmation of a free-radical mechanism for the oxidation of cellulose by atmospheric oxygen in an alkaline medium (14).

Golova has reportedly (17) shown that the oxidation of cellulose is retarded by decomposition products of the aldehyde type (autoinhibition), in the presence of lignins, and also by the introduction of known free-radical inhibitors, such as hydroquinone and benzaldehyde.

Soluble products formed from the air oxidation of regenerated cellulose in a 1% sodium hydroxide solution at 100°C. were found to consist of oligosaccharides (mainly cellotriose, cellotetraose, and cellopentaose) and low molecular weight compounds of acidic and neutral character (mainly saccharinic acids and their lactones). Paper chromatography confirmed the presence of lactic, dihydroxybutyric (and its lactone) and D-glucosaccharinic acid (15).

Samuelson and coworkers (18-19) have investigated the aldonic acid end-groups in cellulose after oxygen bleaching. Experiments with hydrocellulose and cellulose impregnated with kraft lignin showed that arabinonic, mannonic, and erythronic acid end-groups predominated. Only small amounts of meta-saccharinic acid end-groups were detected. The relative amounts of the various aldonic acids detected were similar to the amounts found after the aging of alkali cellulose (20). Also the decomposition of D-glucosone in oxygen-free dilute sodium hydroxide at 100°C. gives similar amounts of aldonic acids (21). Hence, Kolmodin and Samuelson (19) rationalized that glucosone end-groups are precursors to the aldonic acid end-groups, and that the degradation of cellulose during oxygen bleaching can be explained by the reaction scheme proposed by Haskins and Hogsed (22) for the depolymerization of cellulose during the aging of alkali cellulose. This scheme is shown in Fig. 1.

Studies with Cellulose Models

Golova, et al. (16) attempted to oxidize α- and β-methylglucosides in sodium hydroxide solutions (1%) through which atmospheric oxygen was bubbled at 85°C. No nonvolatile acidic products were detected by paper chromatography after 70 hours reaction. However, the optical rotation fluctuated during reaction and the pH decreased; suggesting that some reaction had occurred.

Brooks (23) observed a large effect of oxygen on the rate of alkaline degradation of methyl β-D-glucopyranoside at 150 and 170°C. In 10% sodium hydroxide solution oxygen increased the reaction rate 18 times at 170°C. and 45 times at 150°C. At pH 10.2, the rate in the presence of oxygen was 64 times that in an oxygen-free solution. He rationalized the effect of oxygen on the basis of a lower activation energy for the oxidative reaction than for alkaline hydrolysis, and proposed the reaction scheme shown in Fig. 2 to account for the reactions involved.

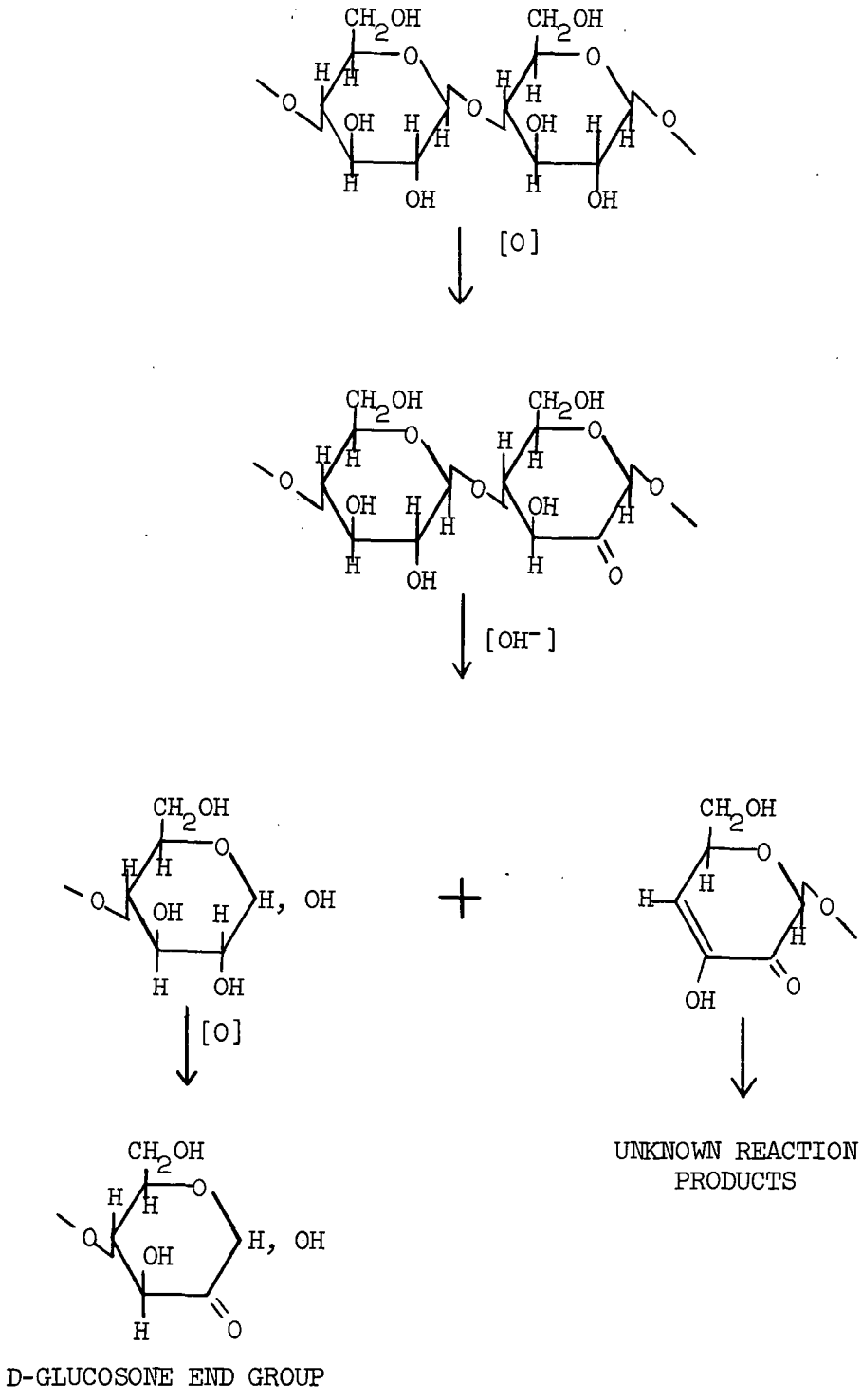

Figure 1. Schematic Representation of the Cleavage of Cellulose Chains According to Samuelson and Thede (20)

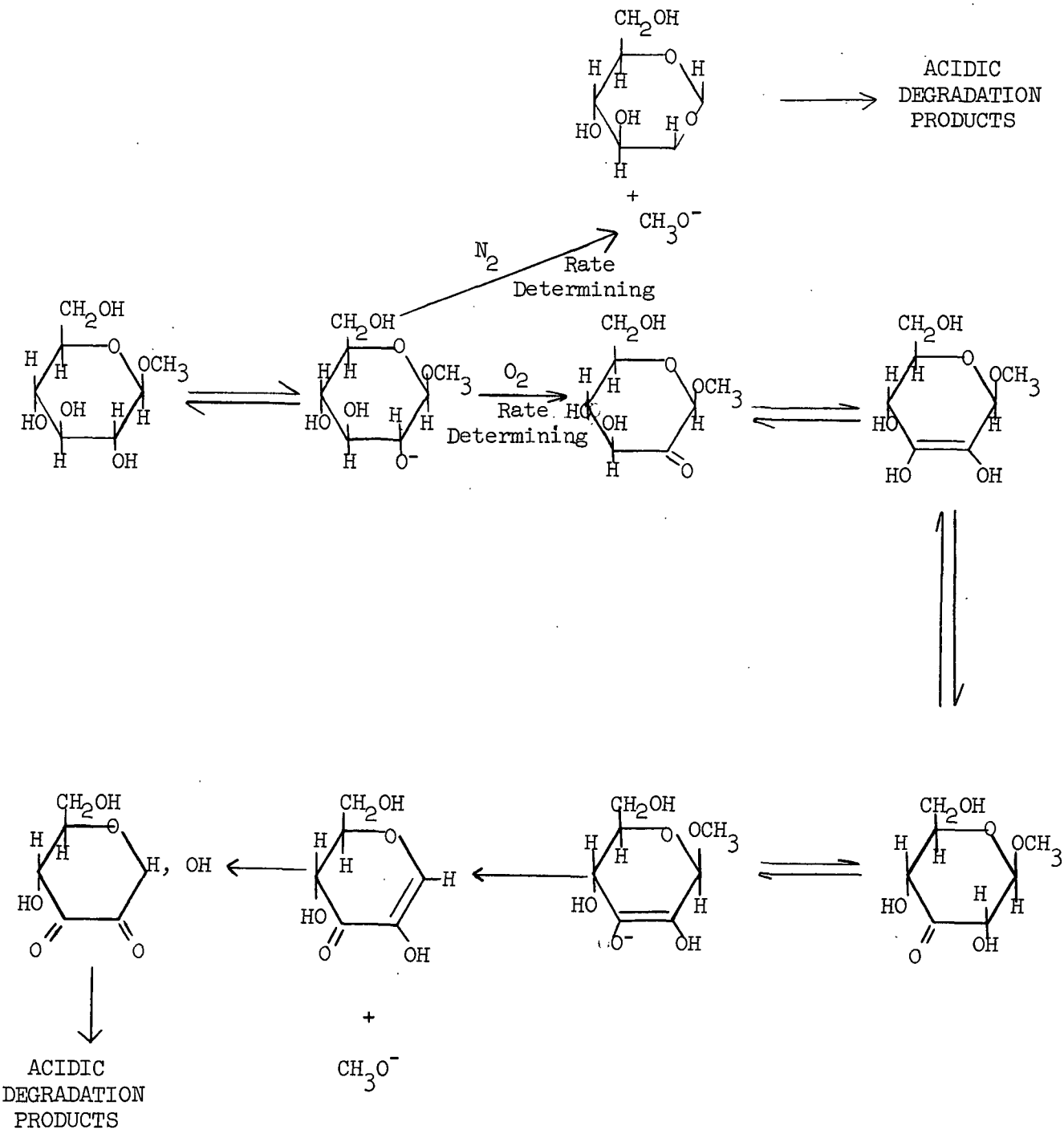

Figure 2. Two Probable Pathways Leading to the Cleavage of the Glucosidic Bond of Methyl β-D-Glucoside in an Alkaline Medium with Molecular Oxygen Present, According to Brooks (23)

Samuelson and Stolpe (24) used cellobiitol as a model substance in studying the degradation of carbohydrates during oxygen bleaching. Oxygen consumption, and the formation of peroxides and organic acids were measured, but direct measurements of cellobiitol degradation were not reported. Glucose and sulfate lignin were found to accelerate the initial consumption of oxygen at 95°C. Glucose accelerated the initial formation of peroxides, and resulted in the formation of larger concentrations of organic acids. Magnesium carbonate depressed the formation of acids even when glucose was present, and lowered the oxygen consumption when either glucose or lignin was present. However, magnesium carbonate increased the maximum concentration of peroxides formed. Thus, magnesium carbonate seems to stabilize the peroxides, thereby preventing them from attacking the cellobiitol.

Cobalt, manganese, copper, and iron reportedly catalyzed the reaction, depending very much on the working conditions (24). Experimental data were not reported for these catalysts.

AUTOXIDATION (AGING) OF ALKALI CELLULOSE

Samuelson (20, 24) has pointed out the similarities between the aging of alkali cellulose and the degradation of cellulose during oxygen bleaching. Both reactions involve cellulose, oxygen, and alkali, but the conditions are quite different as seen in Table I. Despite the differences in reaction conditions, the similarities suggest that the results of investigations of the aging process might eventually help in understanding the degradation of cellulose during oxygen bleaching and vice versa.

TABLE I

TYPICAL PROCESS CONDITIONS FOR OXYGEN BLEACHING AND THE AGING OF ALKALI CELLULOSE

	Oxygen Bleaching (6)	Aging (25)
Cellulose, %	8[a]	30
Sodium hydroxide, %	1	15
Water, %	91	55
Oxygen pressure, atm.	10-15	less than 1 (air)
Temperature, °C.	90-130	25-35

[a]Value given for pulp. Actual cellulose content will depend on the type and yield of pulp used.

The aging (oxygen oxidation) process has been the subject of numerous investigations, yet the reaction mechanisms involved are still debatable. Entwhistle, et al. (25-26) proposed a mechanism involving free-radical intermediates. Mattor (27), unable to detect free radicals, favored an ionic mechanism. MacDonald (28) showed that neither of these mechanisms explains all the facts known about the aging reaction, although both are partly correct. He then advanced a new theory which combined the two. All three mechanisms require the initial oxidation of the reducing group in cellulose; none of them considers the possibility of direct oxidation of the hydroxyl groups along the cellulose chain as the initial oxidation. However, Haskins and Hogsed (22) have considered this possibility. In view of the work of Samuelson and Stolpe (24), Golova, et al. (14), and Brooks (23), direct oxidation of hydroxyl groups in the cellulose chain must be considered a likely route of degradation under oxygen bleaching conditions.

OBJECTIVES OF THESIS

The main objective of this investigation was to gain information about the reactions of cellulose during oxygen bleaching. Special emphasis was placed on some factors thought to be important in chain scission reactions. In an attempt to simplify the study, an approximate model of the building unit of cellulose, methyl β-D-glucopyranoside, was used instead of cellulose itself. The effects of oxygen, sodium hydroxide, and temperature on the kinetics of the degradation of the glucoside was of special interest. The influence of certain glucoside hydroxyl groups on the reaction rate was also of interest.

Brooks' mechanism (Fig. 2) requires the formation of an alkoxide ion before oxidation will occur. Samuelson's scheme (Fig. 1), on the other hand, does not explicitly show the need for an ionized hydroxyl group. Since the C2 hydroxyl group would be expected to be the most easily ionized, it should be particularly important, if an alkoxide ion is indeed required. Oxidation at the C3 and C4 positions might also be important.

Oxidation of the C6 hydroxyl could lead to an inductive effect which would make the glucosidic bond more sensitive to alkaline cleavage. This effect would be analogous to that discussed by Robins (29) for the alkaline hydrolysis of the glucosidic bond of methyl α-D-glucuronoside.

SELECTION OF THE REACTION SYSTEM

MODEL COMPOUNDS

Methyl β-D-glucopyranoside was selected as the primary cellulose model compound for this study, because it is easily obtained in pure form, is soluble

in alkaline solutions, and has many potentially useful derivatives which can be synthesized by proven methods (30). In addition, Brooks (23) has already shown that the alkaline hydrolysis, per se, of methyl β-glucoside is much slower than its oxidation, and at 120° or below hydrolysis would be expected to be insignificant relative to the oxidation rate. Therefore, the oxidative reactions could be studied under oxygen bleaching conditions without the additional complication of alkaline hydrolysis.

Although model studies generally simplify the experimental work, some information about the real reactions cannot be obtained from the model studies. In this case, it is conceivable that cellulose might react at a different rate than methyl β-glucoside. This particular model cannot yield any information about the possible cleavage of the carbon (4)-oxygen bond of cellulose. For this reason, a disaccharide model, e.g., methyl β-cellobioside or 1,5-anhydrocellobiitol, would be preferred. Such models would, of course, introduce additional complications into the studies. Consequently, they would be more appropriately employed in subsequent investigations after some of the fundamental relationships have been established through studies with the simpler monosaccharide models. For similar reasons, the effects of lignin and hemicelluloses, which would be expected to be important to the rate of degradation of cellulose during bleaching, were not studied in this preliminary investigation.

A number of derivatives of methyl β-glucoside were chosen for use in investigating the dependence of the reaction rate on some of the hydroxyl groups of the model. Hydroxyl groups were either "blocked" with methyl ether groups or replaced with hydrogen. These models were: methyl tetra-O-methyl β-D-glucopyranoside, methyl 3,4,6-tri-O-methyl β-D-glucopyranoside,

methyl 3-O-methyl (α,β)-D-glucopyranoside, methyl 2-deoxy β-D-arabinohexopyranoside (or methyl 2-deoxy β-D-glucopyranoside), methyl 6-deoxy β-D-glucopyranoside, and methyl β-D-xyloside.

Since all of the models used had the pyranose ring form, the term "glucopyranoside" will often be referred to as simply "glucoside."

REACTORS

Preliminary attempts were made to use glass reaction vessels and reflux conditions, and to bubble oxygen through the solutions. Maximum temperature and oxygen pressure were necessarily limited, and under these conditions the reaction rates were inconveniently slow. Also, products of the attack of the alkali and oxygen on the glass, presumably silicates, interfered with the glucoside analyses. In addition complete recovery of the methanol generated from the cleavage of the glucosidic bonds was difficult, since it involved stripping the methanol from the oxygen gas stream.

Metal reactors offered the solution to the problems associated with glass vessels, but, because of the possibility of corrosion and, consequently, the effect of metals on the reaction being studied, it was necessary to line the reactors with an inert material. Kel-F[1] and teflon[2] were the only lining materials known to be capable of withstanding the reaction conditions.

A batch-type reactor from which samples could be taken at desired time intervals was preferred, but such a reactor presented problems for which no

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[1] Kel-F is the 3M Company's trademark for poly (chlorotrifluoroethylene).

[2] Teflon is Dupont's trademark for their fully fluorinated polyolefins. Poly(tetrafluoroethylene), TFE, and perfluoro ethylene-propylene copolymer, FEP, were both tested.

satisfactory solution was available at the beginning of this investigation. Sampling the system for methanol would have required a means of obtaining adequate samples of both the liquid and vapor phases when the reactor was hot and under full pressure, and this was not available. Also, lining this type of reactor would have been a difficult task at the time. Now, however, with the techniques that were developed to line the reactors used in this work and other promising methods which have appeared in the past year, this author feels confident that a suitable reactor could be constructed. A schematic drawing of a possible design is shown in Appendix VII. In consideration of the problems expected with the batch-type reaction vessels, tube-type reactors were chosen instead. The reactors were made of 1-inch I.D. pipe, with a valve at one end and sealed at the other. The volume of the reactors was large enough to ensure adequate oxygen pressure during reaction without having to use excessively high pressures. The inside surfaces of the reactors were lined with teflon and Kel-F.

Separate reactors were used for each reaction time. They were cooled before opening; thus, sampling for methanol involved taking a sample of the solution only. It was not necessary to sample the vapor phase.

REACTION CONDITIONS

Reaction conditions were selected such that temperatures and oxygen pressures were in the range of values employed in oxygen bleaching. Glucoside concentrations of ca. 0.01M were chosen for convenience. The glucoside/sodium hydroxide/oxygen ratios were selected such that the alkali and oxygen concentrations would not change significantly during the first 25 to 50% of reaction.

CONSTRUCTION OF REACTORS

Eight tube-type reactors of the same size were used in this work. Each was constructed from a 21-inch long piece of seamless stainless steel pipe, 1 inch I.D., to which flanges had been welded. A typical reactor is sketched in Fig. 3. The pipe section was lined with a sleeve of thin-walled (0.05-inch), flexible teflon tubing flared at the ends. A valve was attached to a Kel-F-coated, flanged adapter unit bolted to one end. The other end was sealed with a teflon disk gasket backed by a metal plate. A small hole drilled through the plate prevented pressure buildup between the gasket and plate.

The valves were custom designed to allow for ease of filling and pressurizing the reactors, and, also, to provide positive sealing during heating and cooling of the reactors, as well as while at constant temperature. Each valve has a floating, nonrotating stem. The disk is made of teflon. A neoprene "O" ring surrounds the teflon disk, and provides the initial gas-tight seal, in case the teflon does not seal immediately. In the closed position the stem is under spring pressure in order to prevent leaks which would arise should the teflon flow. Brass was used for the metal components to minimize the work involved in machining them. A thin film of high-temperature silicone grease was applied to the internal metal surfaces, especially the threads, to serve as a lubricant and to trap any fine, brass particles which might be formed by abrasion; thus, preventing them from contaminating the reaction solutions.

The details of constructing the reactors, the techniques developed for lining them, and some of the major difficulties encountered in the process are described in Appendix I.

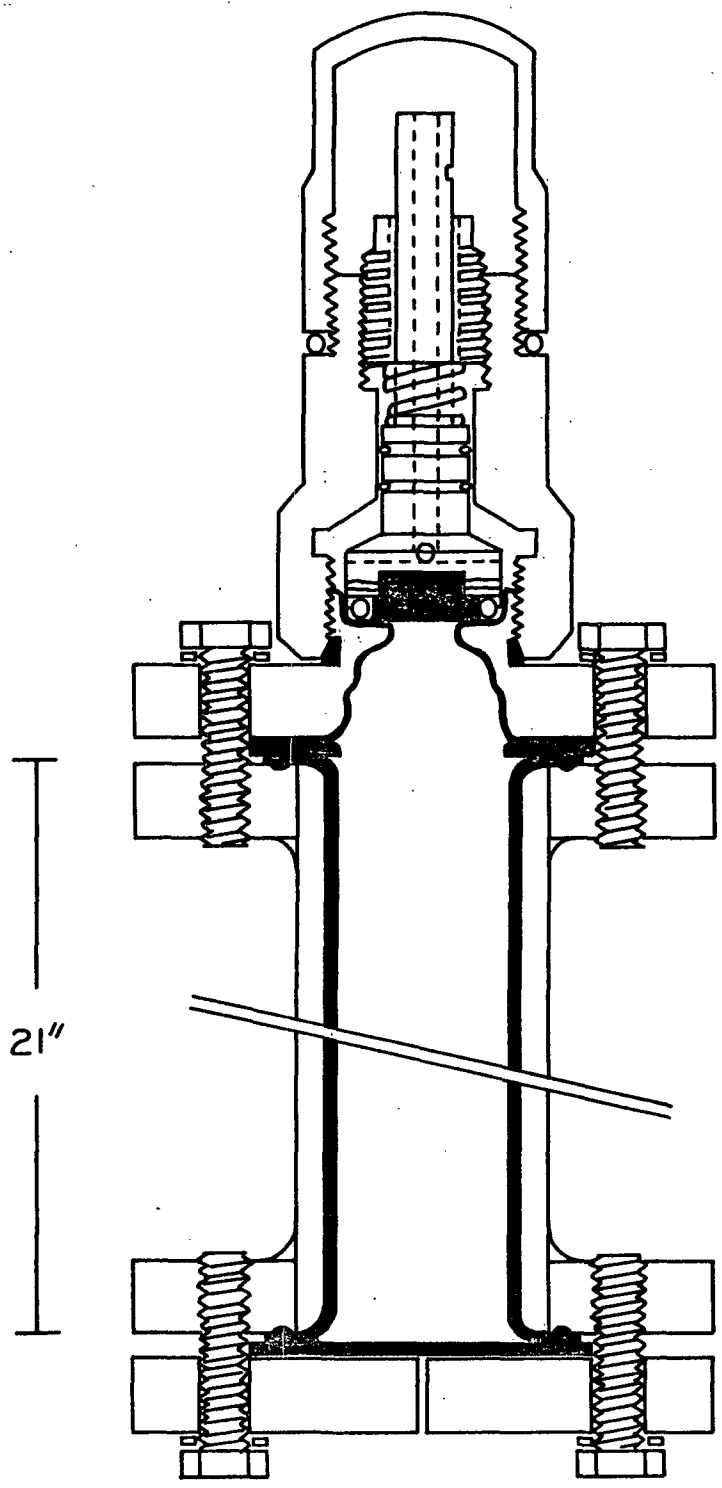


Figure 3. Cross-Sectional View of Assembled Reactor Sketched to Actual Size Except for Chamber Length (21 Inches). Six Flange Bolts Used at Each End

The internal volume of each reactor is about 245 ml. Normally 30 ml. of reaction solution, 0.01M with respect to the glucoside, were placed in each reactor, allowing 215 ml. of space for oxygen. After purging the gas space with oxygen and pressurizing at 25°C. to 60 p.s.i. (74.5 p.s.i.a.), the molar ratio of oxygen to glucoside was 159:1, or, at 34.5 p.s.i.a., 76:1. With 1.25N sodium hydroxide, the molar ratio of alkali to glucoside was 125:1; or 50:1 with 0.5N sodium hydroxide.

The reaction solution reached temperature in less than 14 minutes when the reactor was placed in a 120°C. bath. It cooled to 25°C. in less than 12 minutes when the reactor was immersed in 12°C. water. From the rates of reaction determined later it was evident that less than 0.5% reaction could occur in 26 minutes at 120°C. Therefore, it was not necessary to correct the data for the heating and cooling periods.

GENERAL DESCRIPTIONS OF MATERIALS AND METHODS

Only brief descriptions are given in this section. Detailed descriptions of materials and methods are given in Appendix II and Appendix III, respectively.

PURITY OF MATERIALS

All water was doubly distilled. Sodium hydroxide solutions were carbonate-free. Oxygen purity was at least 99.6%.

The purity of the glycosides used in this work was determined from melting points, optical rotations, and gas-liquid partition chromatography (GLC). All were at least 99.9% pure, except methyl 2-deoxy β-D-glucoside. The latter compound had less than 2% impurities, identified by GLC as the α-glucoside and α- and β-2-deoxy glucose. The relative concentrations did not change even after treatment with oxygen and alkali; hence, it is doubtful that the impurities affect the reaction of the β-glucoside.

FILLING THE REACTORS

The glucoside was dissolved in a solution of 1.25N sodium hydroxide to make a solution of the desired concentration of glucoside (usually 0.01M). For runs at lower sodium hydroxide concentrations, the alkaline solution was first diluted.

With the valve removed, each reactor was purged with oxygen by means of a glass delivery tube extending to the sealed end of the reactor. An aliquot (30 ml.) of the reaction solution was added and the valve replaced without its cover. The oxygen supply was connected to the valve, the system pressurized, and the valve closed. The oxygen line was disconnected, and the valve cover

was replaced. Then, the reactors were shaken and placed in a hot oil bath for the time desired.

OIL BATH AND QUENCH TANK

An oil bath containing 70 gallons of Texaco Regal K heat transfer oil was used to heat the reactors. The bath was equipped with a recirculating pump to provide uniform temperature throughout. The temperature was controlled within $\pm$ 0.5°C. by means of an iron-constantan thermocouple connected to a Honeywell/ Brown Pyr-O-Vane automatic temperature controller. Accurate temperature measurement was made with a Brooklyn "high precision" calibrated thermometer.

The reactors were placed on a rack assembly in the oil bath. A motor drive rocked the assembly,and caused the reactors to be tilted to 30 degrees above and below the horizontal at the rate of 3 cycles per minute. This motion provided adequate mixing so that diffusion of the oxygen into the solution did not control the rate of reaction.

At the end of the reaction time the reactor was transferred to a tank of water at about 10-15°C. When the reactor was cooled, the pressure was released, and the valve was removed. The reaction solution was poured into a glass bottle which was subsequently sealed until the sample was analyzed.

ANALYSES OF REACTION SOLUTIONS

Unreacted glucoside was determined by gas-liquid partition chromatography using the internal standard method. Compounds which were not sufficiently volatile were first converted to their trimethylsilyl ether derivatives.

Methanol liberated from the glucoside was determined by a colorimetric method using chromotropic acid.

Peroxides were determined by the standard iodometric method.

RESULTS AND DISCUSSIONS

PERFORMANCE OF REACTORS

COMPARISON OF DATA FROM DIFFERENT REACTORS

Since the data obtained at each reaction time came from separate reactors, it was necessary to determine the error in the data caused by differences in the reactors. This was done with methyl β-glucoside (0.01M) in sodium hydroxide (1.25N) under typical experimental conditions, i.e., 30 ml. of solution per reactor and 60 p.s.i.a. O_2. All reactors were heated simultaneously at 120°C. for 25 hr. 20 min., and the reaction solutions were analyzed for methanol and unreacted glucoside.

The results are shown in Table II. It is seen that, after about 22% reaction, the maximum deviation of the glucoside values is +1.4% of the original glucoside concentration. On the same basis, the maximum deviation of the methanol concentration is -2.1%. It should be noted that these are maximum values and include analytical errors as well as errors caused by differences in the reactors.

DURABILITY OF REACTORS

In general, the reactors worked well. The values were virtually trouble-free. The "O" rings became embrittled from prolonged exposure to the heat and oxygen, but they were usable for at least two hundred hours of operation including a number of heating cycles. Replacement, when required, was very easy. The durabilities of the teflon sleeves in the reaction chambers and of the Kel-F coatings on the valve adapters were variable. Sometimes they lasted for several hundred hours without developing breaks. In a few cases, linings broke after

only a few hours of use. The life of the teflon sleeve depended greatly on the quality of the flared ends and on the pressure applied at the flanges. The durability of the Kel-F coating seemed to depend on factors determined by the coating technique; e.g., thickness, uniformity, number and size of pores, stress concentrations, and degree of crystallinity of the film.

TABLE II

COMPARISON OF REACTORS

Reactor No.	MBG[a], mmole/liter	Methanol, mmole/liter	MBG + Methanol, mmole/liter
1	7.808	1.392	9.200
2	7.868	1.339	9.207
3	7.839	1.376	9.215
4	7.743	1.364	9.107
5	7.882	1.188	9.070
6	7.939	1.060	8.999
7	7.859	1.106	8.977
8	7.698	1.351	8.993
Average	7.830	1.272	9.096
Range	0.241	0.332	0.238
Maximum deviation	+0.136	-0.212	
Standard deviation	0.0778	0.133	0.121

[a] Methyl β-D-glucoside.

STABILITY OF METHANOL

The stability of methanol was checked under several conditions approximating those used in the kinetic runs. The results, shown in Table III, demonstrate the stability of methanol. There was no significant loss of methanol, even when the initial methanol concentration was nearly 100 times the maximum normally released during the glucoside runs.

TABLE III

STABILITY OF METHANOL

(Sodium hydroxide, 1.25N; temperature, 120°C.)

Initial Methanol, mmoles/liter	Reaction Time, hr.	Methanol Found, mmoles/liter
(Oxygen, 43 p.s.i.a.)		
184	0	184.3
184	50	184.3
184	50	184.3
1.90	0	1.91
1.90	0	1.83
1.90	69	1.89
1.90	69	1.96
(Oxygen, 64.5 p.s.i.a.)		
2.03	0	2.04
2.03	50.5	2.02

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

KINETICS

General Methods of Data Treatment

At this time a brief review of general methods of treating kinetic data might be helpful for the ensuing discussion. It is assumed that the reader is familiar with basic kinetics terminology which is found in introductory texts on reaction kinetics, such as Laidler's (31), on which the following review is based.

There are two main methods of treating kinetic data; the method of integration and the differential method. The first method employs the integrated form of the rate equation for an assumed reaction order. It is the most widely used, but has a major drawback in that it is something of a "hit-and-miss" method; one must first guess as to the reaction order, and then see whether the guess fits the experimental results. Reactions whose rates do not depend on reactant concentrations raised to simple powers cannot be treated satisfactorily by the method of integration, which may in fact lead to quite erroneous conclusions (31). For example, a first-order reaction that is inhibited by products as they are formed may appear to be a second-order reaction if the method of integration is used.

The differential method, on the other hand, in which the differential, or unintegrated, form of the rate equation is employed, is theoretically quite straightforward, and, unlike the integration method, does not lead to any particular difficulties when there are complexities in the kinetic behavior. In this method values of the reaction rate are obtained from plots of concentration vs. time by taking slopes. The main difficulty of this

method is determining the slopes accurately. In spite of this drawback, the method on the whole is more reliable than the integration method.

The differential method may be applied in two different ways. The initial rates may be measured at various initial reactant concentrations, and the logarithm of the rate may be plotted against the logarithm of the concentration. The slope of the plot then gives the order with respect to concentration, or the true order, since it relates to initial conditions and is not interfered with by reaction intermediates (32).

The other way of employing the differential method involves considering a single run, and measuring slopes at various times, corresponding to a number of values of the reactant concentration. A plot of the logarithm of the rate against the logarithm of the concentration then gives the order with respect to time. Reaction intermediates may interfere with the order determined in this way.

When complications exist, or are suspected, it is more satisfactory to employ the differential method, and to deal first only with initial rates. Plots of the logarithms of the initial rates against the logarithms of the initial concentrations may or may not be straight lines, but in either case the dependence becomes apparent (31).

Method of Treating Glucoside Data

The present investigation constitutes the first known study of the degradation of methyl β-D-glucoside under oxygen bleaching conditions. Hence, there was no explicit information available to help guide this study. Preliminary investigations of the reaction kinetics, showed that the method of integration was not adequate for treating the data. Therefore, the differential

method using initial rates was used in the subsequent studies. The rate equations used (including the integrated equations used in preliminary analyses) will be developed in this section.

When only glucoside, oxygen, and sodium hydroxide were present, it was assumed that the reaction would obey the basic rate expression (1).

$$-d[G]/dt = k[G]^a\ [O_2]^b\ [NaOH]^c \qquad (1)$$

where $-d[\underline{G}]/d\underline{t}$ = rate of disappearance of glucoside

$\underline{k}$ = rate coefficient

$[\underline{G}]$ = concentration of glucoside

$[O_2]$ = concentration of oxygen

$[NaOH]$ = concentration of sodium hydroxide

$\underline{a},\underline{b},\underline{c}$ = orders with respect to the corresponding reactants

If oxygen and sodium hydroxide are in large excess, their concentrations will remain nearly constant, and Equation (1) can be simplified to

$$-d[G]/dt = k'[G]^a \qquad (2)$$

where $k' = k\ [O_2]^b\ [NaOH]^c$.

Determination of Order by the Integration Method

The integrated form of (2) depends on the assumed order, $\underline{a}$. The following three integrated equations are obtained for values of $\underline{a}$ corresponding to 1, 1.5, and 2. $[\underline{G}]_o$ represents the initial glucoside concentration.

$$a = 1;\ \ln[G] - \ln[G]_o = k_1'\ t \qquad (3)$$

$$a = 1.5;\ 2(1/[G]^{0.5} - 1/[G]_o^{0.5}) = k'_{1.5}\ t \qquad (4)$$

$$a = 2;\ 1/[G] - 1/[G]_o = k_2'\ t \qquad (5)$$

From these equations it is easily seen that a simple reaction which is first-order in glucoside will give a linear plot of $\ln[\underline{G}]$ against $\underline{t}$. A plot of $1/[\underline{G}]^{0.5}$ against $\underline{t}$ will be linear if the order in glucoside is 1.5. A second-order dependence on glucoside will give a linear plot of $1/[\underline{G}]$ against $\underline{t}$.

Determination of Order by The Differential Method

The differential method employing initial rates is based on the differential rate Equation (1) written in terms of the initial conditions.

$$v_i = k[G]_i^a \, [O_2]_i^b \, [NaOH]_i^c \qquad (6)$$

where $\underline{v_i}$ = initial reaction velocity = $-d[\underline{G}]/d\underline{t}$

$[\ ]_{\underline{i}}$ = initial concentration of reactant

The order in glucoside, $\underline{a}$, is obtained by varying the initial glucoside concentration while maintaining oxygen and sodium hydroxide constant. Under these conditions Equation (6) can be simplified to Equation (7).

$$v_i = k''[G]_i^a \qquad (7)$$

where $k'' = k \, [O_2]_i^b \, [NaOH]_i^c$.

Taking logarithms

$$\log v_i = \log k'' + a \log [G]_i \qquad (8).$$

Thus, the slope of a plot of the logarithm of the initial rate against the logarithm of the initial glucoside concentration gives the order in glucoside.

The reaction orders relative to the other reactants can be obtained in a similar fashion by varying their initial concentrations in turn while keeping other reactant concentrations constant, and using Equations (9) and (10).

$$\log v_i = \log k''' + b \log [O_2]_i \qquad (9)$$

where $k''' = k [G]_i^a [NaOH]_i^c$

$$\log v_i = \log k^{IV} + c \log [NaOH]_i \qquad (10)$$

where $k^{IV} = k [G]_i^a [O_2]_i^b$.

Preliminary Kinetic Run

A preliminary reaction run was made in order to establish the general nature of the reaction. Oxygen and sodium hydroxide were in large excess so their concentrations would not vary appreciably during the run. The reaction was carried out until about forty percent of the glucoside was degraded. The data for the unreacted glucoside and methanol liberated are presented in the concentration vs. time plot shown in Fig. 4, from which several important aspects of the reaction are immediately evident. The rate of liberation of methanol is slower than the rate of degradation of the glucoside throughout the reaction time studied. Since methanol was previously shown to be stable under the reaction conditions, this phenomenon suggests that degradation of the glucoside does not result in immediate cleavage of the glucosidic bond, in other words, some methanol must remain bound to the degraded glucoside, at least in some cases.

In addition, there is no observable induction period or sign of autocatalysis in either the glucoside degradation or the methanol liberation. It would appear, then, that the data might be satisfactorily treated by the method of integration.

The glucoside data in Fig. 4 were plotted according to the integrated rate Equations (3), (4), and (5) for assumed orders in glucoside of 1, 1.5, and 2, respectively. The results (Fig. 5) clearly show that the kinetic data

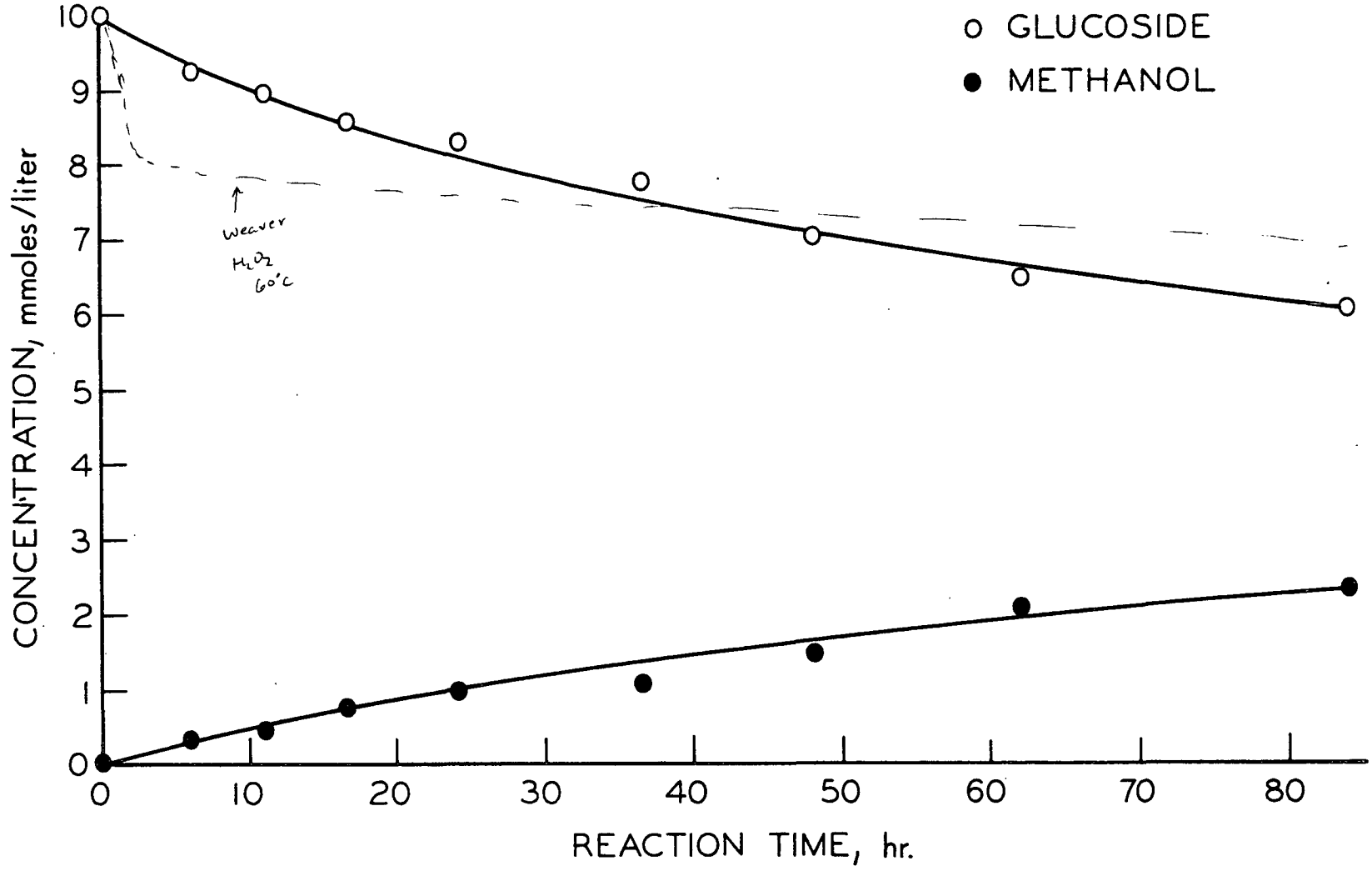


Figure 4. Degradation of Methyl β-D-Glucoside and Formation of Methanol at 120°C. in 1.25N Sodium Hydroxide and Oxygen, 43 p.s.i. at 25°C.

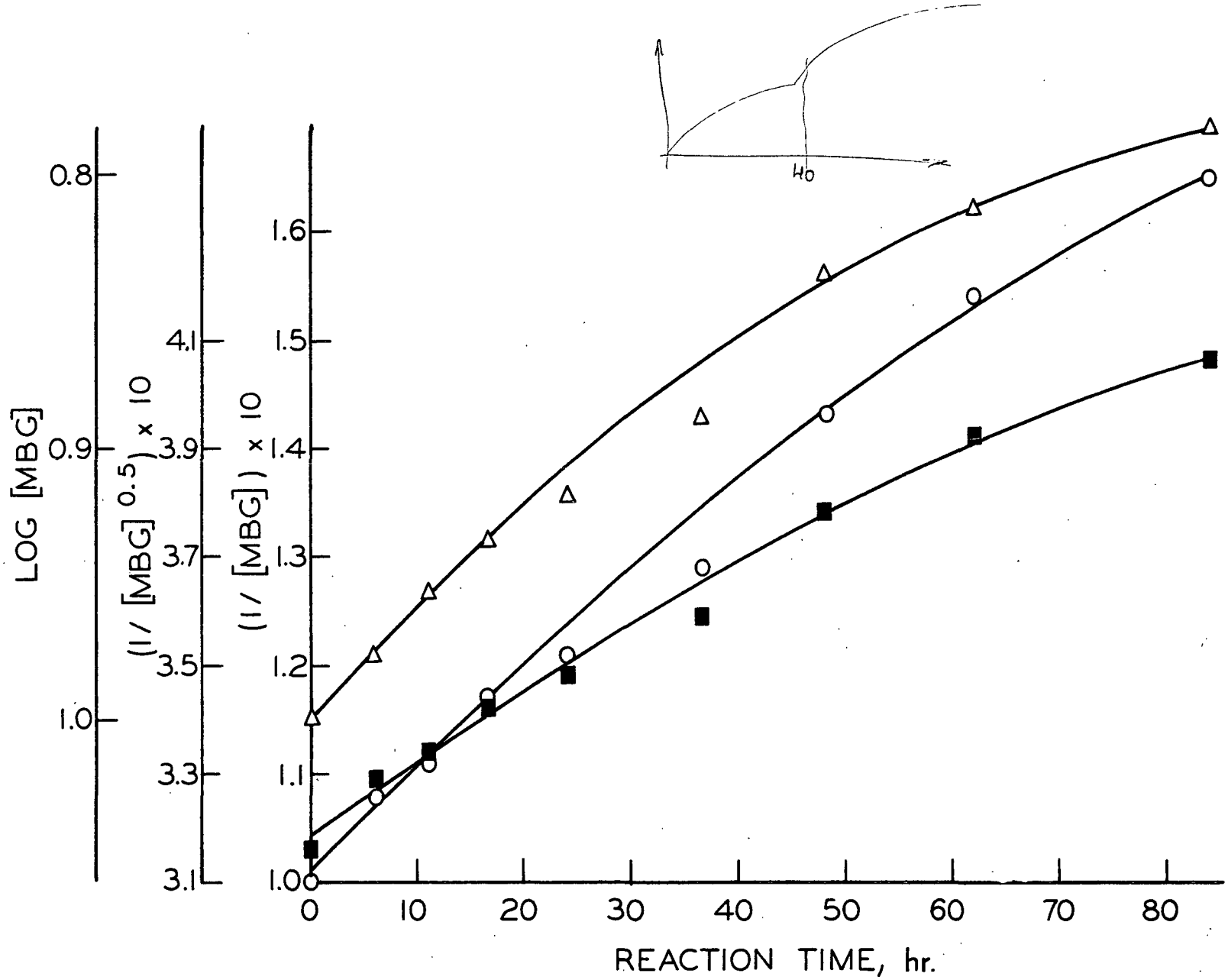


Figure 5. Degradation of Methyl β-D-Glucoside. Data of Fig. 4 Plotted for for Assumed Reaction Orders of 1.0 (Δ), 1.5 (■), and 2.0 (○)

are not amenable to treatment by the method of integration. None of the curves are linear. All deviate in the direction which indicates that the reaction is slowing down faster than predicted by the rate expressions. This phenomenon suggests that products are inhibiting the reaction. Therefore, as discussed previously, the differential method would be more appropriately employed in this case. The data from subsequent reactions were treated by the differential method using initial rates which were obtained from the slopes of tangents to the concentration-time curves at zero time. The curves were drawn on large plots in order to minimize the errors involved in determining the slopes.

The initial rates of glucoside degradation for the conditions studied are summarized in Table IV. The kinetic data including ratios of methanol formed to glucoside reacted are tabulated in Appendix VI.

Effect of Glucoside Concentration

The rate of degradation of glucoside depends on the initial glucoside concentration as shown in Fig. 6. The data plotted according to Equation (8) shows that the reaction has a second-order dependence on the initial glucoside concentration.

Effect of Oxygen Pressure

In investigating the effect of oxygen on the reaction rate, the question arises whether Henry's Law [Equation (9)] holds under the experimental conditions used.

$$O_2 = P_{O_2}/H \qquad (11)$$

where O_2 = oxygen in solution

P_{O_2} = partial pressure of oxygen

H = Henry's Law Constant.

TABLE IV

SUMMARY OF INITIAL REACTION RATES

Glucoside[a]	Glucoside Concn., mmoles/liter	Sodium Hydroxide Concn., N	Oxygen Pressure, p.s.i.a.	Temperature, °C.	Initial Rate,[b] mmoles/liter/hr.
MBG	10.00	1.25	74.5	120	0.110
MBG[c]	10.01	1.25	74.5	120	0.226
MBG	10.46	1.25	74.5	120	0.120[e]
MBG	10.46	1.25	0	120	0.000
MBG	29.02	1.25	74.5	120	0.959
MBG	9.98	1.25	54.5	120	0.0838
MBG	10.00	1.25	34.5	120	0.0528
MBG	10.01	0.875	63.7	120	0.0675
MBG[d]	10.01	0.875	63.7	120	0.176
MBG	9.99	0.50	54.5	120	0.0436
MBG	10.01	1.25	74.5	110	0.0528
MBG	10.00	1.25	74.5	99	0.0242
MTMBG	10.01	1.25	74.5	120	0.00129
M346MBG	10.00	1.25	74.5	120	0.0178[f]
M6DBG	10.01	1.25	74.5	120	0.0701[f]
MBX	9.95	1.25	74.5	120	0.0984
M2DBG	10.00	1.25	0	120	0.00327
M2DBG	9.99	1.25	74.5	120	0.158
M3MG	9.78	1.25	74.5	120	0.0441[g]

[a] Abbreviations:
MBG: Methyl β-D-glucoside
MTMBG: Methyl tetra-O-methyl β-D-glucoside
M346MBG: Methyl 3,4,6-tri-O-methyl β-D-glucoside
M6DBG: Methyl 6-deoxy β-D-glucoside
MBX: Methyl β-D-xyloside
M2DBG: Methyl 2-deoxy β-D-glucoside
M3MG: Methyl 3-O-methyl (α,β)-D-glucoside

[b] Initial rate = $-d[MBG]/dt$ at $t = 0$.

[c] Glucose added, 0.15 mmole/liter.

[d] Hydroquinone added, 0.21 g./liter.

[e] Inflection in curve; average rates = given. Initial rate = 0.0849.

[f] Inflection in curve; average rates = given. Initial rate = 0.0280.

[g] Inflection in curve; average rates = given. Initial rate = 0.0312.

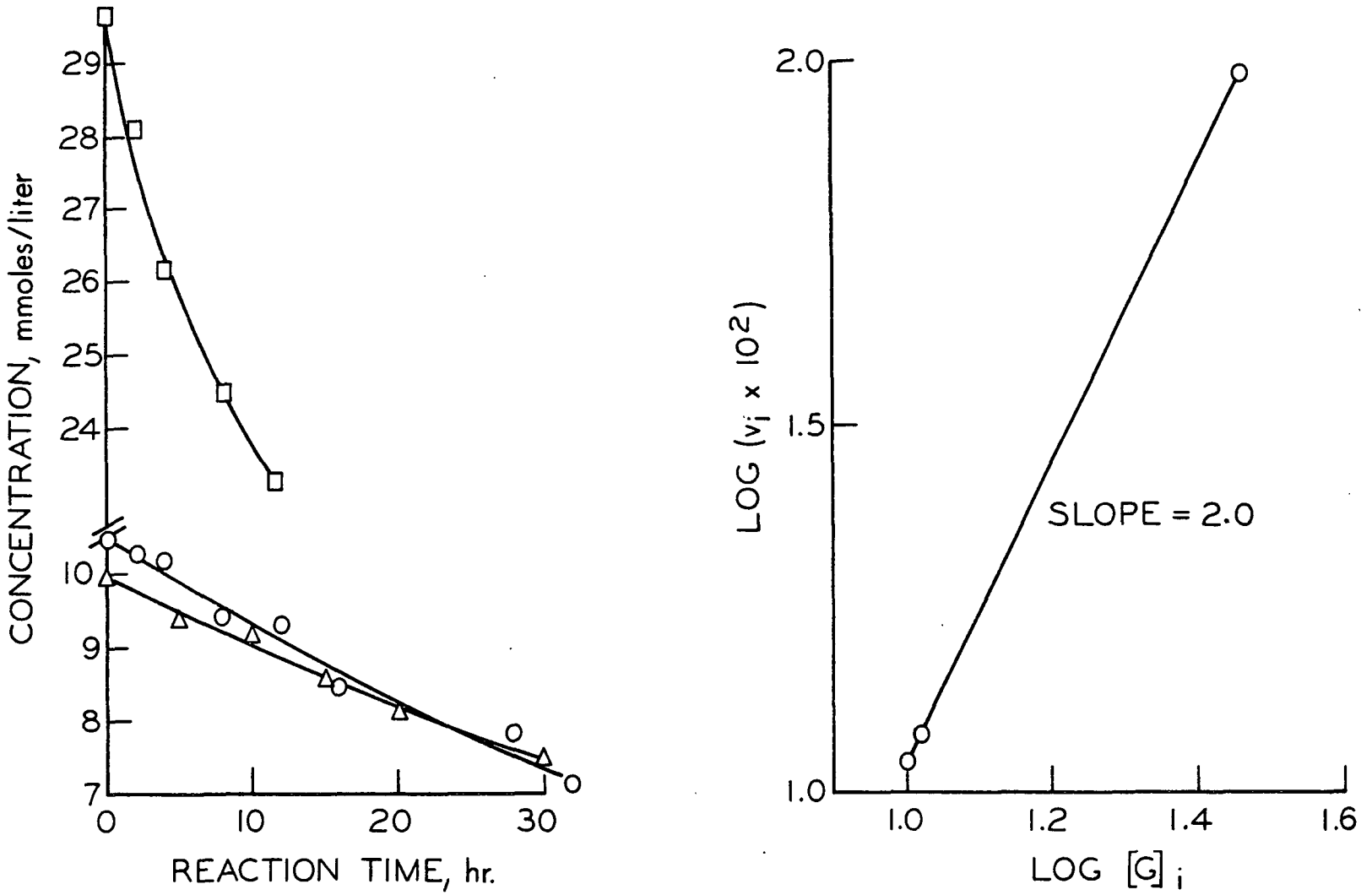


Figure 6. Effect of Initial Glucoside Concentration on the Rate of Degradation of Methyl β-D-Glucoside in 1.25N Sodium Hydroxide at 120°C. with 74.5 p.s.i. Oxygen (at 25°C.)

No experimental data could be found in the literature to verify this assumption. However, Frolich, et al., (33) found the solubility of oxygen in water to be a linear function of oxygen pressure in the range of 0 to 70 atm. The presence of sodium hydroxide in the solution will change Henry's Law constant (34), but would not be expected to affect the linearity of the relationship at constant alkali concentration. Therefore, it is reasonable to assume that Henry's Law applies in this work, since only the oxygen pressure was varied.

Varying the initial oxygen pressure changes both the rate of glucoside degradation and the rate of liberation of methanol as illustrated in Fig. 7. The rate of methanol generation is always less than the rate of glucoside degradation when oxygen is present.

There is essentially no reaction in the absence of oxygen, as would be predicted from an extrapolation of Brooks' data (23). The liberation of a small amount of methanol when nitrogen replaced the oxygen in the reactor can be attributed to traces of oxygen which remained in solution, since the solutions were not purged with nitrogen.

A plot of the logarithm of the initial rate of glucoside degradation against the logarithm of the oxygen pressure is linear with a slope of 0.95 (Fig. 7). Thus, according to Equation (9) and assuming Henry's Law holds, there is approximately a first-order dependence on oxygen for the rate of reaction of glucoside.

Effect of Sodium Hydroxide Concentration

The initial sodium hydroxide concentration affects the rate as shown in Fig. 8. In all cases, it is seen that the methanol is liberated more slowly than the glucoside reacts.

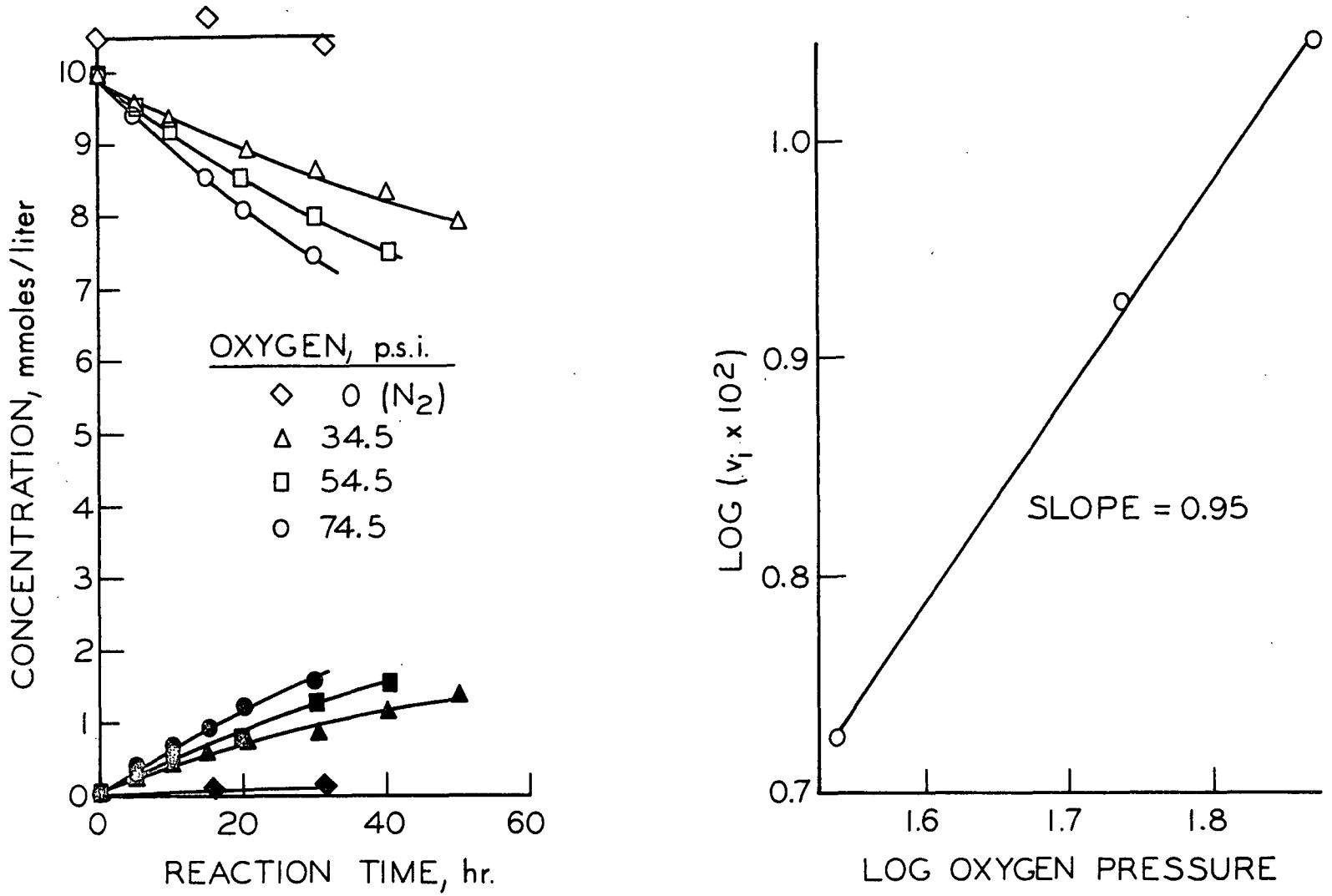


Figure 7. Effect of Oxygen Pressure on the Rate of Degradation of MBG in 1.25N Sodium Hydroxide at 120°C. Shaded Symbols: Methanol Produced

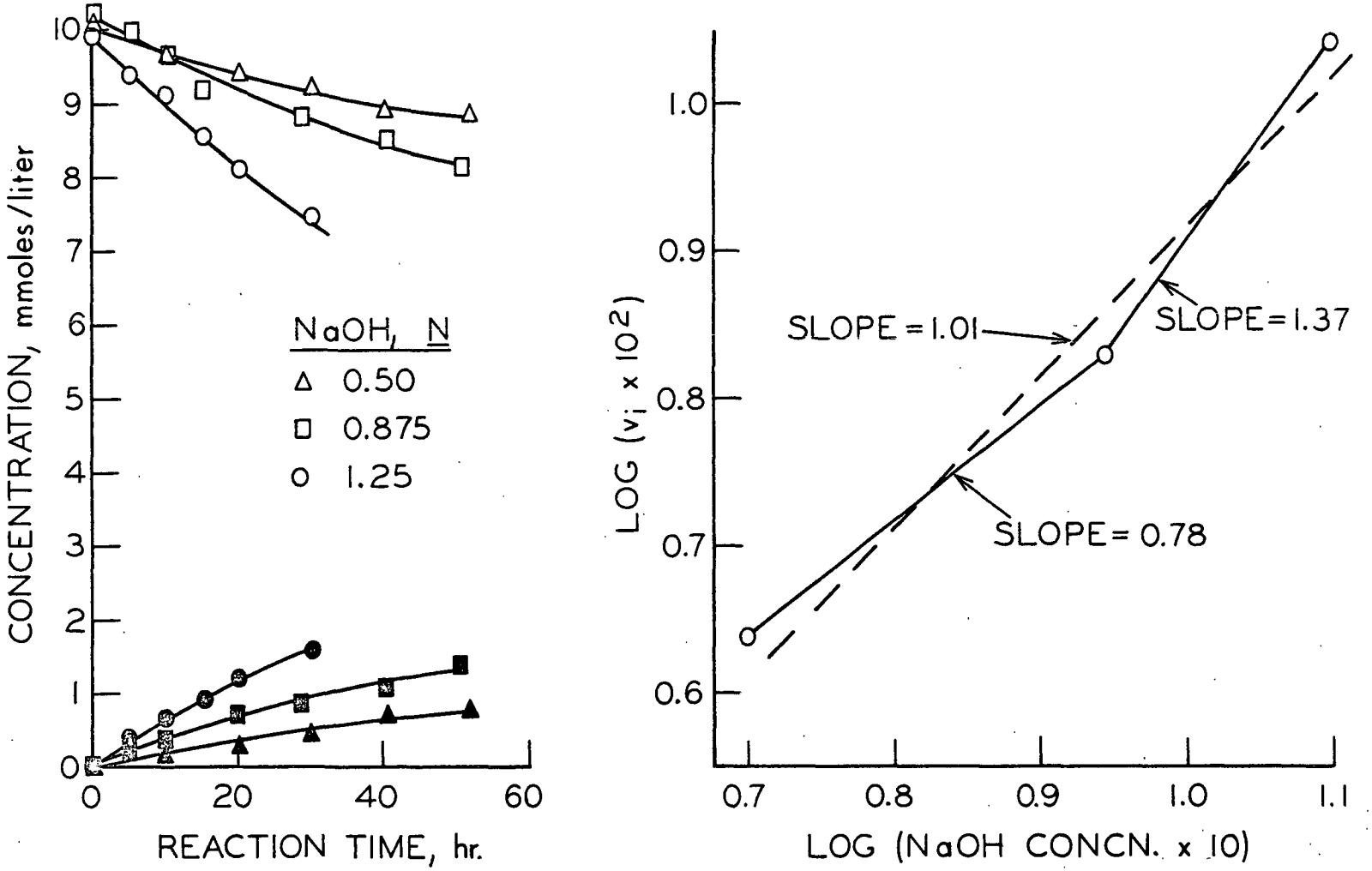


Figure 8. Effect of Sodium Hydroxide Concentration on the Rate of Degradation of MBG at 120°C. with 74.5 p.s.i.a. Oxygen (at 25°C.). Shaded Symbols: Methanol Liberated

The initial rates of reaction of glucoside were plotted according to Equation (10), and a nonlinear plot was obtained as seen in Fig. 8. The best straight-line fit of the data has a slope of 1.01 which suggests a first-order dependence on sodium hydroxide. However, the nonlinearity of the plot suggests a complex dependence on alkali, and deserves further discussion.

There are several possible explanations for the nonlinear dependence found, but none is readily verified experimentally. Multiple reaction pathways having different alkali dependencies could cause a nonlinear dependence on sodium hydroxide. Salt effects might also cause the nonlinearity, since constant ionic strength was not maintained in this work, but not enough is known about the reaction mechanism to permit reasonable speculation regarding the magnitude or direction of such effects, if they exist. In order to study salt effects one would have to first find an innocuous salt to use.

Another possible explanation for the nonlinear dependence relates to possible variations in dissolved oxygen which inadvertently accompanied the variations in initial alkali concentration. It is well known that the solubility of a gas in a solution is a function of the type and pressure of the gas, the temperature, and the type and concentration of the solute (35). Therefore, in order to vary the alkali concentration without simultaneously altering the oxygen concentration in solution, one must know the relationship between these parameters. This is not well defined for the particular experimental conditions used in this work. Consequently, it was necessary to establish an approximate relationship from the little data that are available. The data of Bruhn, et al. (34) span the conditions of interest, and were interpolated for the temperature and alkali concentrations used in

this study. From these data the oxygen pressures required to give equal oxygen concentrations for the various sodium hydroxide concentrations were as described in Appendix V. Because of possible errors in the estimations, the oxygen concentrations may not have been, in fact, equivalent. In this event, the apparent dependence of the rate on sodium hydroxide would necessarily include a factor to account for inequalities in the oxygen concentration.

Effect of Temperature

The rate of reaction of methyl β-D-glucoside depends on temperature in the range 99-120°C. as illustrated in Fig. 9. The apparent activation energy determined from the initial rates is 21 kcal./mole. It is interesting to note that this is the same value obtained by Entwhistle, et al. (25) for the aging of alkali cellulose over the temperature range of 5-80°C. The correspondence tempts one to think that the mechanisms are similar, but there is not yet sufficient evidence to prove that they are in fact the same.

At all three temperatures used in the present work, methanol is released more slowly than the glucoside is degraded, but there is no indication that the degradation and glucosidic bond cleavage reactions have different temperature dependencies.

Effect of Hydroxyl Groups

General

The influence of certain hydroxyl groups of methyl β-D-glucoside on its rate of reaction is illustrated in Fig. 10. Blocking any one of the hydroxyl groups at C2, C3, or C6, changes the rate of reaction. There is virtually no reaction when all hydroxyl groups are blocked with methyl ether groups as in methyl tetra-O-methyl β-D-glucoside. This clearly demonstrates that the reaction requires one or more free hydroxyl functions on the molecule.

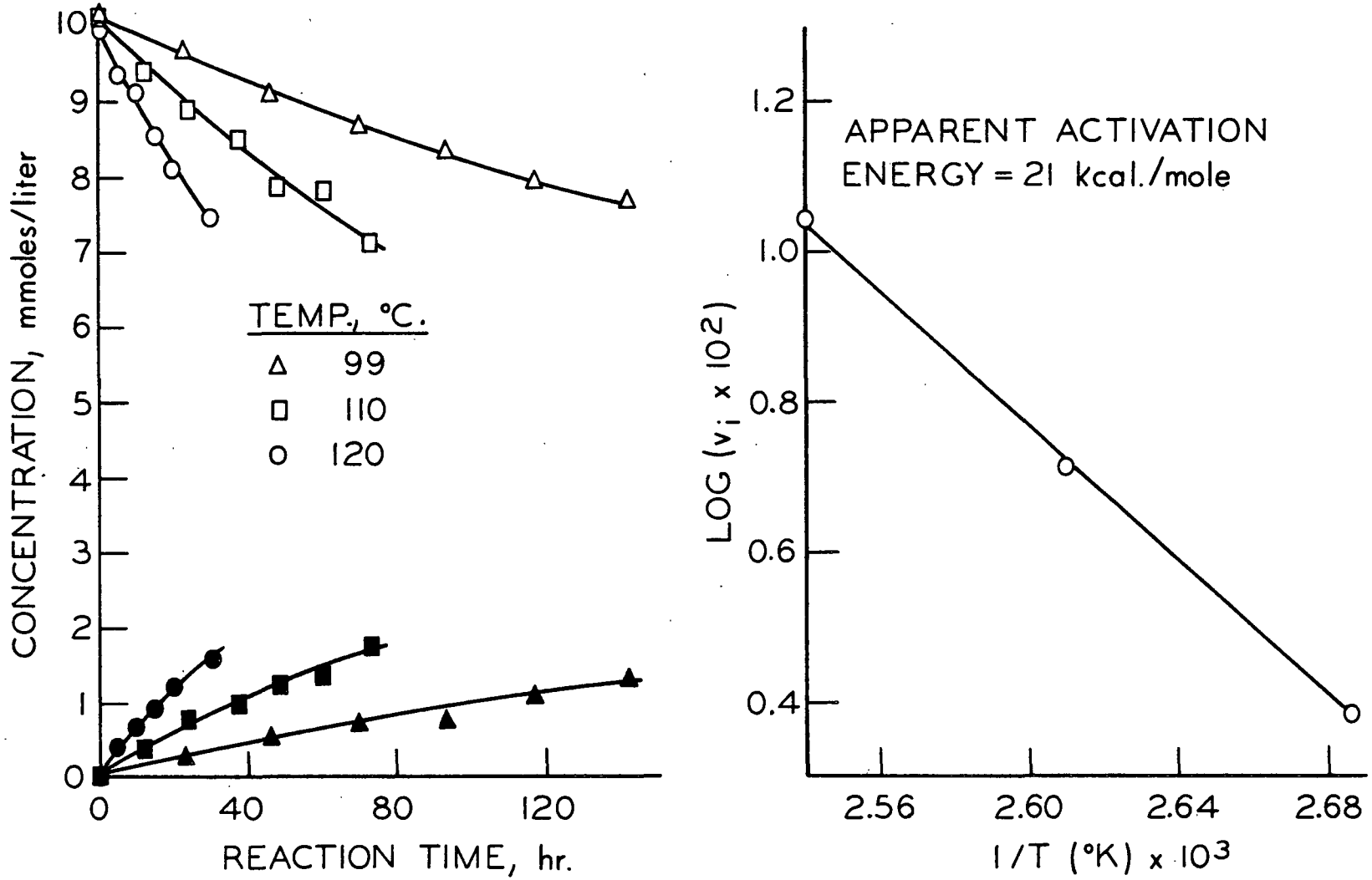


Figure 9. Effect of Temperature on the Rate of Degradation of MBG in 1.25N Sodium Hydroxide with 74.5 p.s.i. Oxygen (at 25°C.). Shaded Symbols: Methanol Produced

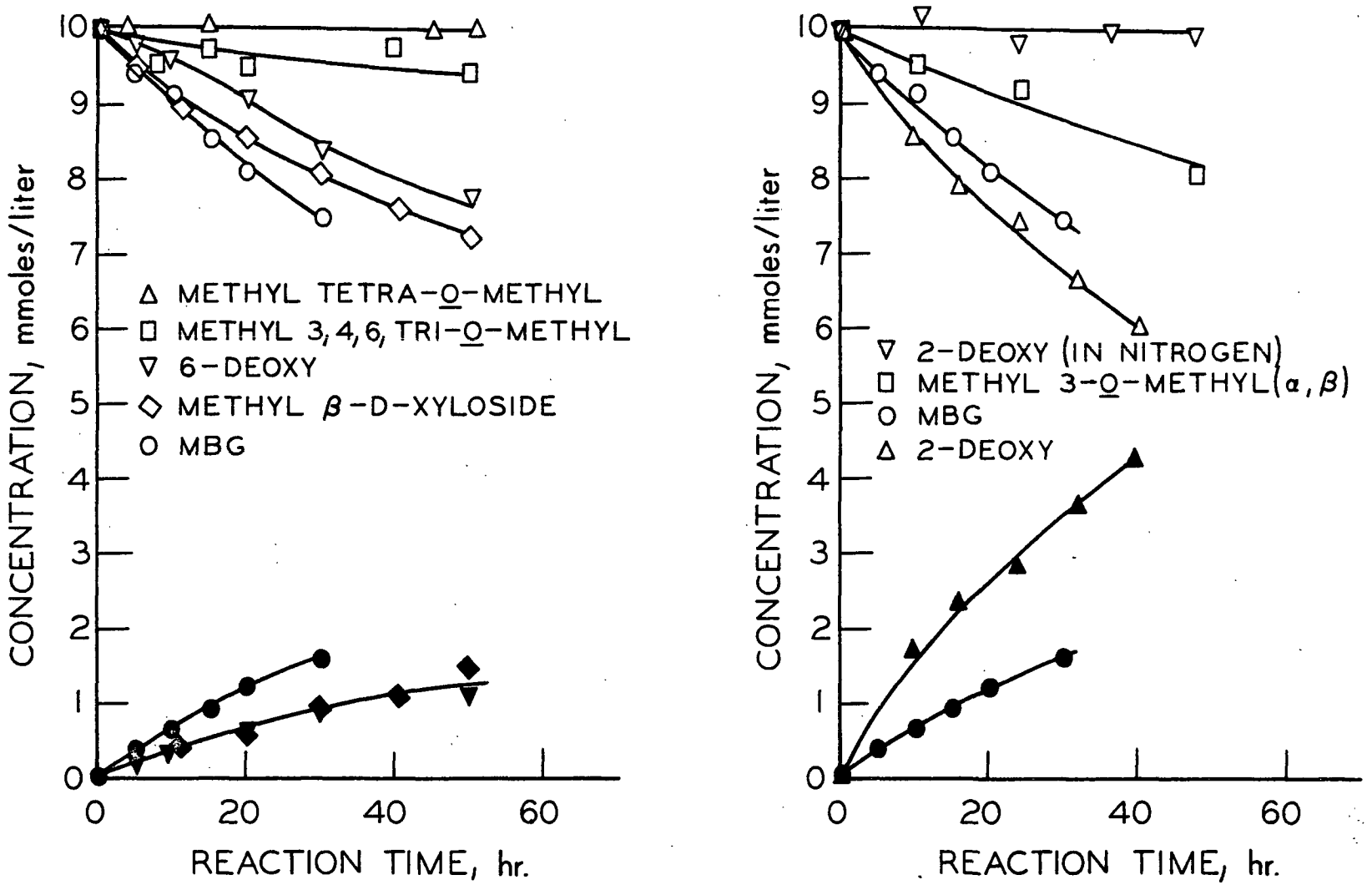


Figure 10. Influence of Hydroxyl Group Functions on the Degradation of Methyl β-D-Glucoside in 1.25N Sodium Hydroxide at 120°C. with 74.5 p.s.i. Oxygen (at 25°C.). Shaded Symbols: Methanol Liberated

C6 Hydroxyl Group

The relative unimportance of the C6 hydroxyl group was determined through a comparison of the reaction rates of methyl β-D-glucoside and two of its analogs which lack the C6 hydroxyl: methyl 6-deoxy β-D-glucoside and methyl β-D-xyloside. As seen in Fig. 10, the two compounds lacking the C6 hydroxyl group react slightly more slowly than methyl β-D-glucoside, and both liberate methanol more slowly than they react, indicating that reaction occurs, at least in part, through a pathway which results in the formation of relatively stable products to which methanol is still bound. This phenomenon is the same as was observed in all reactions of methyl β-D-glucoside.

The rate of liberation of methanol is the same for both methyl β-D-xyloside and methyl 6-deoxy β-D-glucoside, but the rates of degradation differ slightly. The reason for this difference is presently without explanation.

C2 Hydroxyl Group

Two approaches were employed in studying the effect of the C2 hydroxyl group on the reaction rate of methyl β-D-glucoside. If the C2 hydroxyl is necessary for reaction, blocking all other hydroxyls should have little effect on the rate. Removal of the C2 hydroxyl, on the other hand, would be expected to prevent reaction.

Methyl 3,4,6-tri-O-methyl β-D-glucoside and methyl 2-deoxy β-D-glucoside were chosen as models for this investigation. The former model was found to react much more slowly than methyl β-D-glucoside (Fig. 10). The 2-deoxy model, on the contrary, reacts slightly faster than methyl β-D-glucoside. Clearly, then, the C2 hydroxyl group is not necessary for reaction. Reactions through other hydroxyl groups must also contribute to the overall degradation rate of methyl β-D-glucoside.

The reactivity of the 2-deoxy glucoside was an unexpected result, especially in view of the implied importance of the C2 hydroxyl group in Brooks' postulated mechanism (discussed in the Introduction). At first it was thought that the unexpectedly fast rate was due in part to an appreciable rate of alkaline hydrolysis of the deoxy glucoside, which would contribute to the overall rate of disappearance. This possibility was checked by measuring the rate of disappearance of the compound in the absence of oxygen. The results, given in Fig. 10, show that the rate of alkaline hydrolysis is negligible.

The rate of methanol liberation from the 2-deoxy glucoside is also much faster than would be expected on the basis of other glucosides studied. A mole equivalent of methanol is liberated from methyl 2-deoxy β-D-glucoside, whereas only about one-half mole of methanol was released from each mole of methyl β-D-glucoside, methyl 6-deoxy β-D-glucoside, and methyl β-D-xyloside that reacted.

C3 Hydroxyl Group

Blocking the C3 hydroxyl group caused a significant decrease in the rate of degradation, as demonstrated by methyl 3-O-methyl (α,β)-D-glucopyranoside (Fig. 10). The model used was a mixture of anomers (about 47% β), and since the importance of the anomeric configuration on the reaction rate is not known, it might be erroneous to ascribe the entire rate decrease to blocking the C3 hydroxyl group. However, degradation through reaction at the anomeric carbon appears to be of little importance, since methyl tetra-O-methyl β-D-glucoside does not react. Thus, it seems likely that the decreased rate is mostly, if not entirely, due to blocking the hydroxyl group.

Since there is still an appreciable rate of reaction when the C3 hydroxyl is blocked, reaction through this hydroxyl group accounts for only part of the overall reactivity.

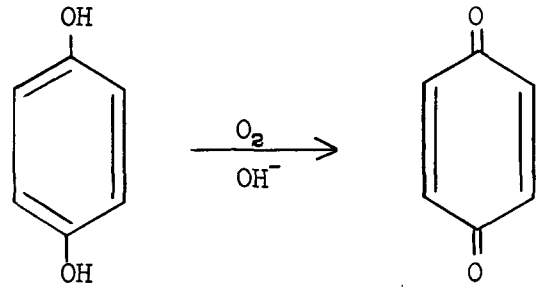
Effects of Additives

Oxidation reactions involving molecular oxygen are often influenced by the presence of "foreign" materials in the reaction medium. Therefore, it was of interest to make preliminary investigations on the effect of some additives on the oxidation of methyl β-D-glucoside. The choice of additives studied and the conditions used in this work were limited. Nevertheless, the results demonstrate the important role that some additives can play in the reaction of methyl β-D-glucoside, and, more importantly, suggest that the many components in a commercial pulp can greatly influence the oxidation of carbohydrates during oxygen bleaching.

Hydroquinone

Hydroquinone was added to a reaction solution with the intention of checking for the existence of a free-radical mechanism, since inhibition by hydroquinone is often taken as evidence that a free-radical mechanism is operative (36). Hydroquinone has been shown to inhibit the oxidation of cellulose by atmospheric oxygen in alkaline media (17, 26), and therefore, might be expected to inhibit the reaction of methyl β-D-glucoside under oxygen bleaching conditions.

Contrary to expectations, hydroquinone greatly increases the reaction rate of the glucoside, as illustrated in Fig. 11. This behavior might be rationalized by considering the oxidation of hydroquinone in alkaline solutions. Quinone and hydrogen peroxide are products (36) [Equation (12)]. In alkaline solution



(12)

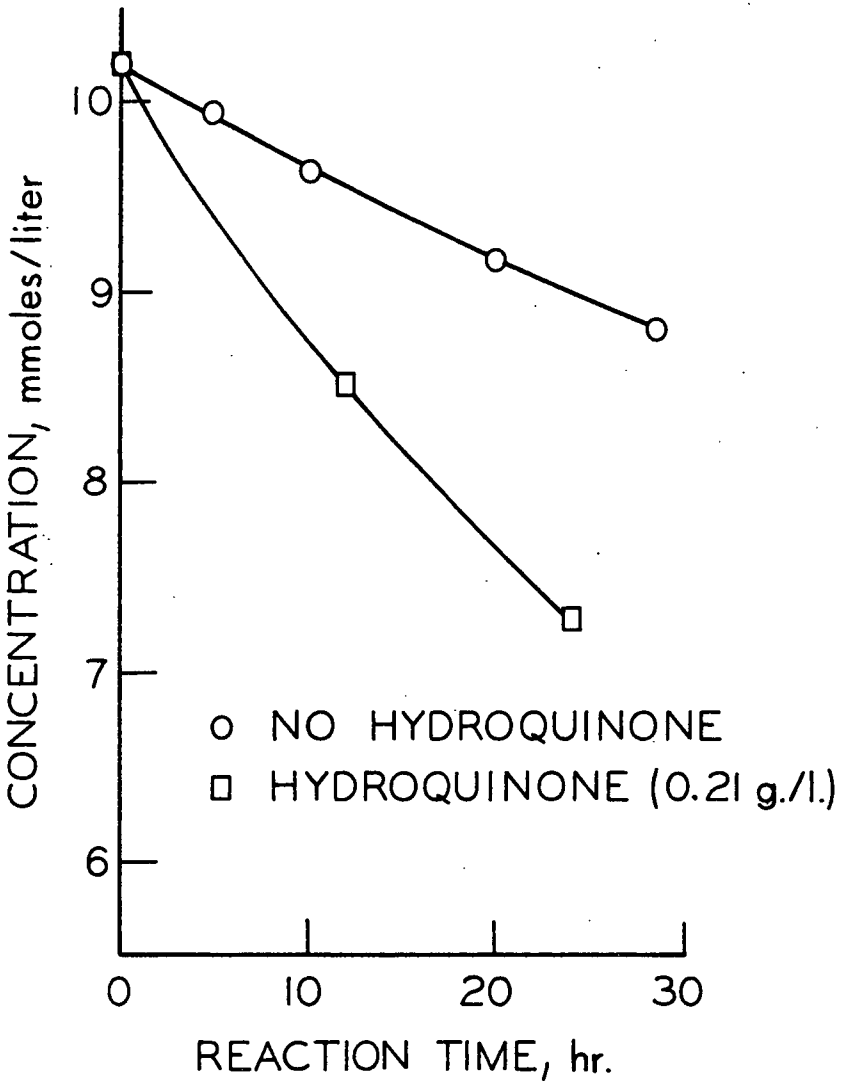


Figure 11. Effect of Added Hydroquinone on the Degradation of MBG. NaOH, 0.875N; 120°C.; Oxygen, 63.7 p.s.i. (at 25°C.)

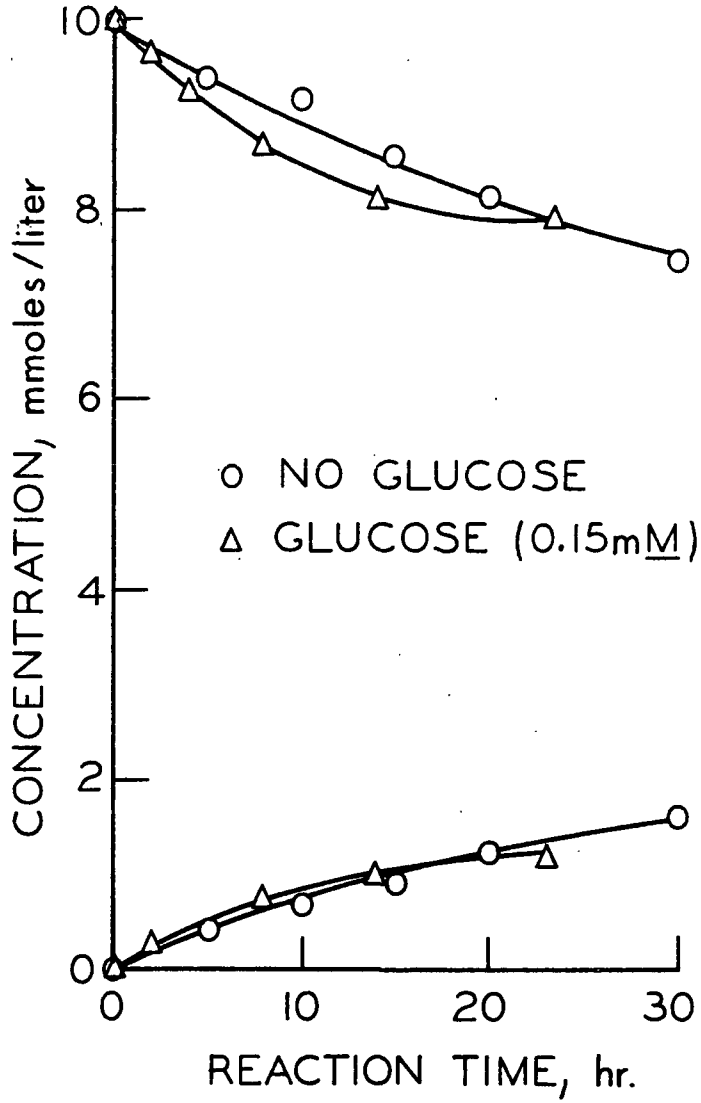


Figure 12. Effect of Added Glucose on the Degradation of MBG. NaOH, 1.25N; 120°C.; Oxygen, 74.5 p.s.i. (at 25°C.)

hydrogen peroxide ionizes readily to form its anion, the perhydroxyl ion, an extremely good

$$H_2O_2 + OH^- \rightleftharpoons HOO^- + H_2O \qquad (13)$$

nucleophile. Wiberg (37) found the perhydroxyl ion to be more reactive than hydroxide by factors as large as 10^4 for a number of typical bimolecular nucleophilic displacement reactions. Thus, perhydroxyl ion generated in the alkaline oxidation of hydroquinone might react rapidly with methyl β-D-glucoside, perhaps through bimolecular nucleophilic displacement of the methoxyl aglucone, and thereby cause the increased rate of reaction.

The increased rate of glucoside degradation observed when hydroquinone was present is significant, because it demonstrates the important role that hydroquinonelike components of wood pulps might play in the degradation of cellulose during oxygen bleaching.

Glucose

Samuelson and Stolpe (24) showed that glucose acted as an initiator in the reaction of cellobiitol under oxygen bleaching conditions. As illustrated in Fig. 12, glucose does affect the degradation of methyl β-D-glucoside. The initial rates of glucoside decomposition and methanol formation are both accelerated. Furthermore, it is seen that glucose has a more pronounced effect on the rate of glucoside degradation than on the liberation of methanol.

It is also noted that in the presence of glucose the initial rate is faster, but, at later times, the rate slows down more rapidly than when glucose is not added. This phenomenon suggests that the initial rapid oxidation of glucose produces active species which in turn attack the glucoside. After the glucose is consumed and the active species disappear, the reaction will slow down to a

rate corresponding to its own oxidation by oxygen. These active species may be peroxides, since they have been shown to be formed from glucose under oxygen bleaching conditions (24). It is reasonable to expect peroxides (e.g., hydrogen peroxide) to accelerate the rate of degradation of glucoside as discussed previously in connection with hydroquinone.

Metal Corrosion Products

Methyl β-D-glucoside is degraded faster in Type 316 stainless steel reactions than in teflon-lined reactors, as the data in Fig. 13 demonstrate. Reaction solutions removed from the stainless steel reactors were colored yellow-green, probably due to the presence of chromate salts in solution. Emission spectroscopy of the solutions showed that iron and small amounts of nickel were present in addition to much larger amounts of chromium. Deposits of oxides of nickel and iron on the reactor walls were readily visible.

It is not possible from this preliminary investigation to draw conclusions regarding the specific metals which catalyze the reaction, or the nature of catalysis, i.e., homogeneous, heterogeneous, or merely apparent catalysis caused by a competing oxidation by the metal oxides. Nevertheless, the observation points out the potential effect of metals on the oxidative reactions.

Magnesium Carbonate

Magnesium carbonate* retards only slightly the rate of reaction of methyl β-D-glucoside, as shown in Fig. 14. A much larger effect would be expected considering the strong inhibitory action it has on the depolymerization of cellulose during oxygen bleaching (2-4). The difference probably lies in the

*Added in the form of $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (1 g./l.).

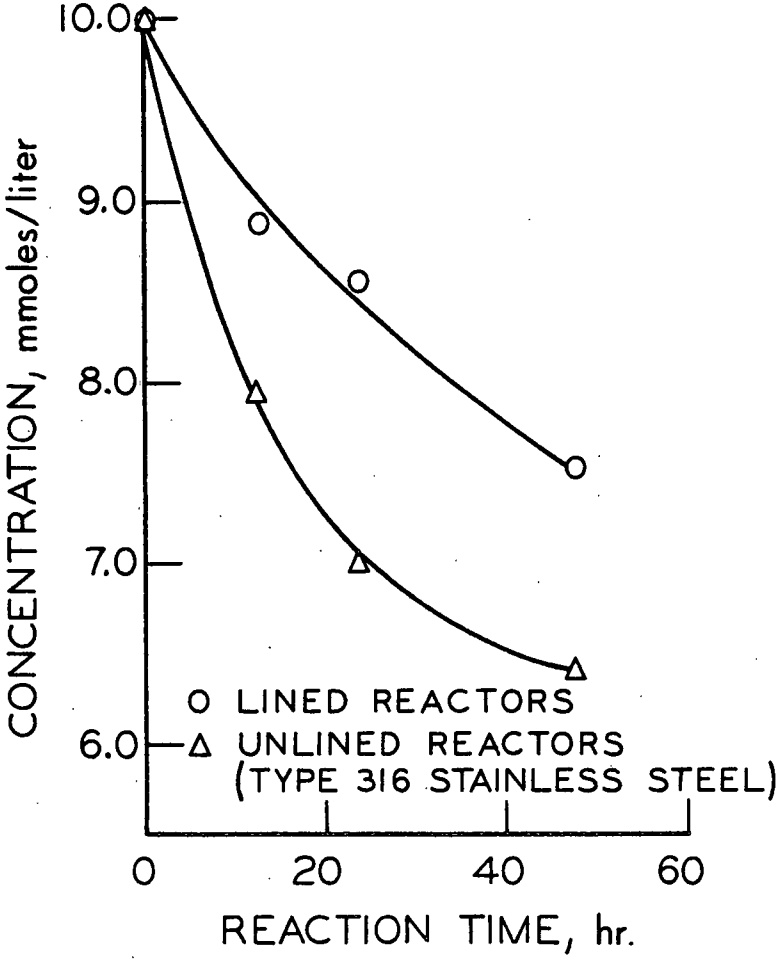


Figure 13. Effect of Reactor Corrosion on the Rate of Degradation of MBG. Sodium Hydroxide, 1.25N; 120°C.; Oxygen, 43 p.s.i. (at 25°C.)

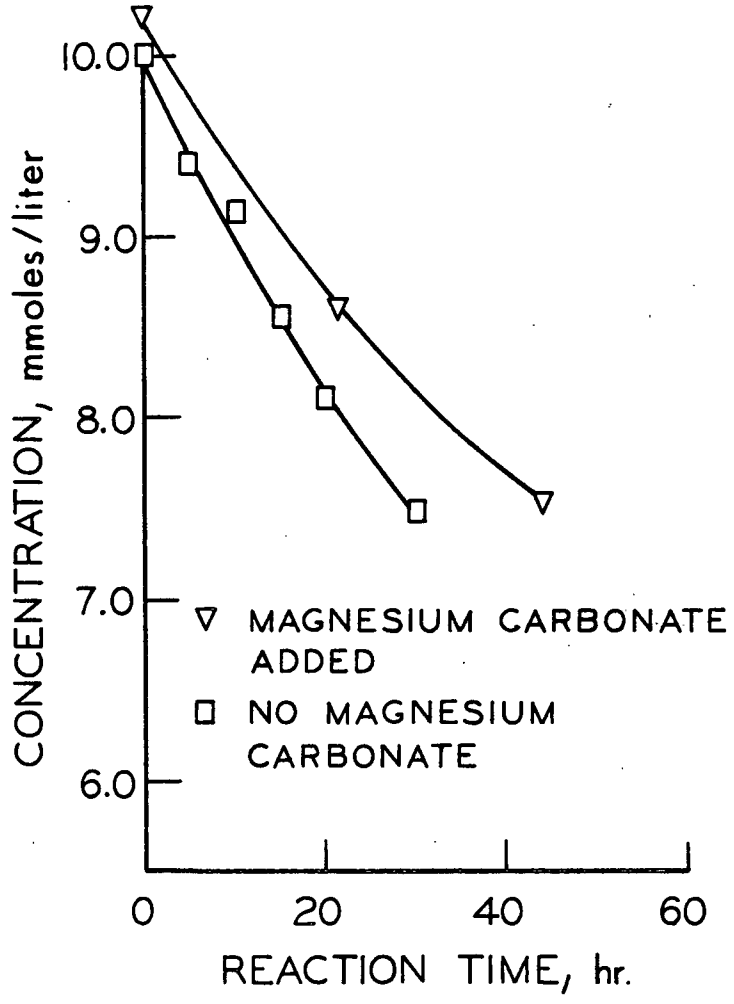


Figure 14. Effect of Magnesium Carbonate on the Rate of Degradation of MBG. Sodium Hydroxide, 1.25N; 120°C.; Oxygen, 43 p.s.i. (at 25°C.). Added $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ 1 g./Liter

retardation of additional reaction pathways for cellulose during bleaching which are not operative in the model system. Discussion of the probable role of magnesium carbonate will be deferred to a later section.

PEROXIDE FORMATION

Peroxides, as measured iodometrically, were detected in the methyl glucoside reaction system at 120°C. None was detected in the absence of the glucoside. Therefore, they must have originated from the reaction of the organic material. Their concentrations were always quite low and considerably below those reported by Samuelson and Stolpe (24) to be formed from cellobiitol under similar conditions (at 95°C.).

To check whether the difference in the amounts of peroxides formed from methyl glucoside and cellobiitol was due to the compounds themselves, reactions were run under identical conditions, and peroxide concentrations were measured after several reaction times. 1,5-Anhydrocellobiitol was also studied simultaneously. It is a disaccharidelike cellobiitol, but has fewer hydroxyl groups. Like methyl β-D-glucoside it lacks a freely rotating acyclic end as has cellobiitol (the glucitol moiety). Thus, if peroxide formation is related to the structure of the compound being oxidized, the level of peroxides formed from 1,5-anhydrocellobiitol would be expected to be intermediate to those of methyl glucoside and cellobiitol.

The amounts of peroxides found in solutions of the three models after various reaction times are plotted in Fig. 15. The corresponding concentrations of unreacted substrate are given in Fig. 16. A comparison of the two figures shows a direct relation between reactivity of the model and peroxide formation.

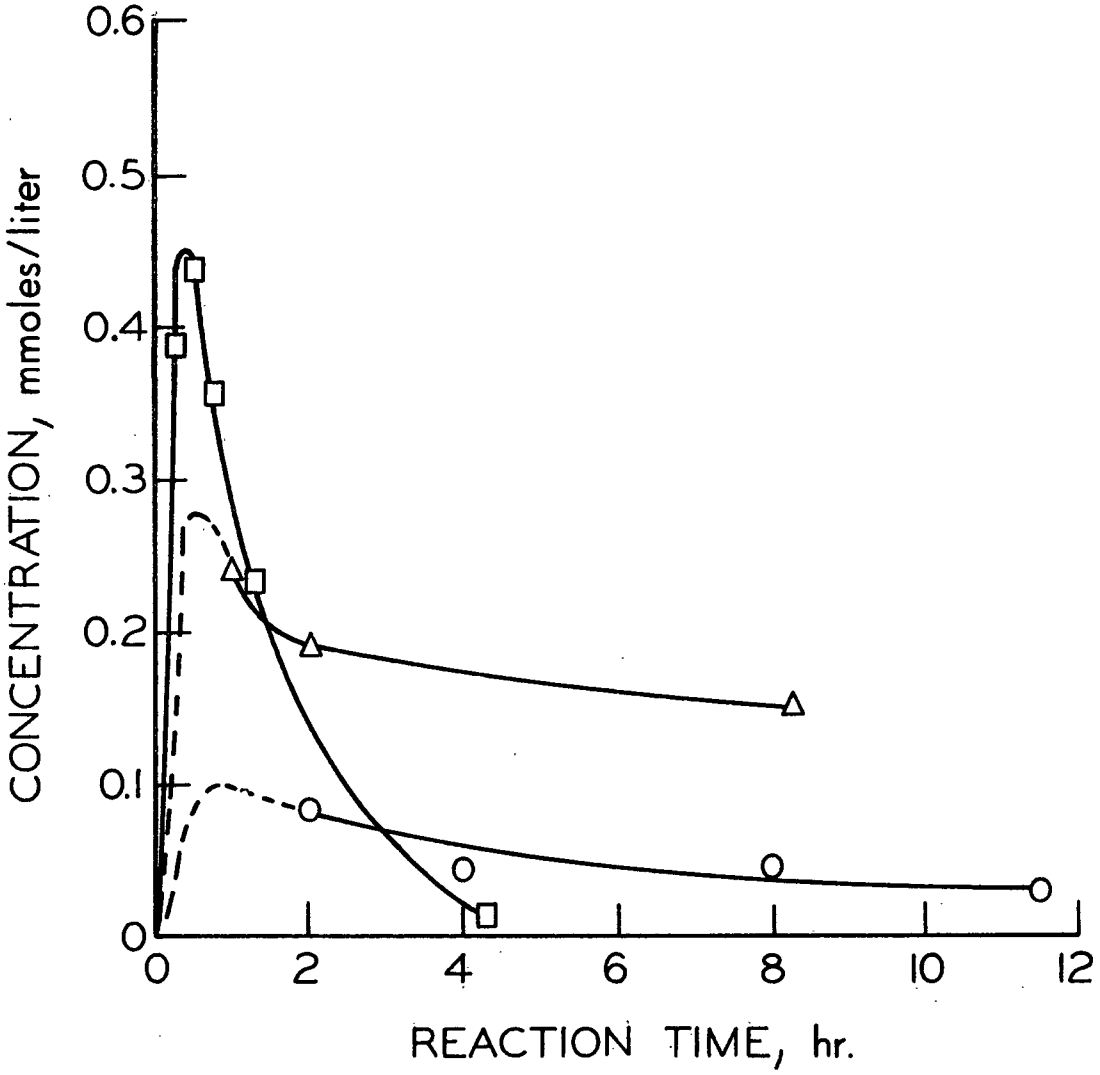


Figure 15. Peroxides Formed During the Degradation of Methyl β-D-Glucopyranoside (O), 1,5-Anhydrocellobiitol (Δ), and Cellobiitol (□) in 1.25N Sodium Hydroxide Containing Oxygen at 120°C. Initial Oxygen Pressure: 74.5 p.s.i.a.

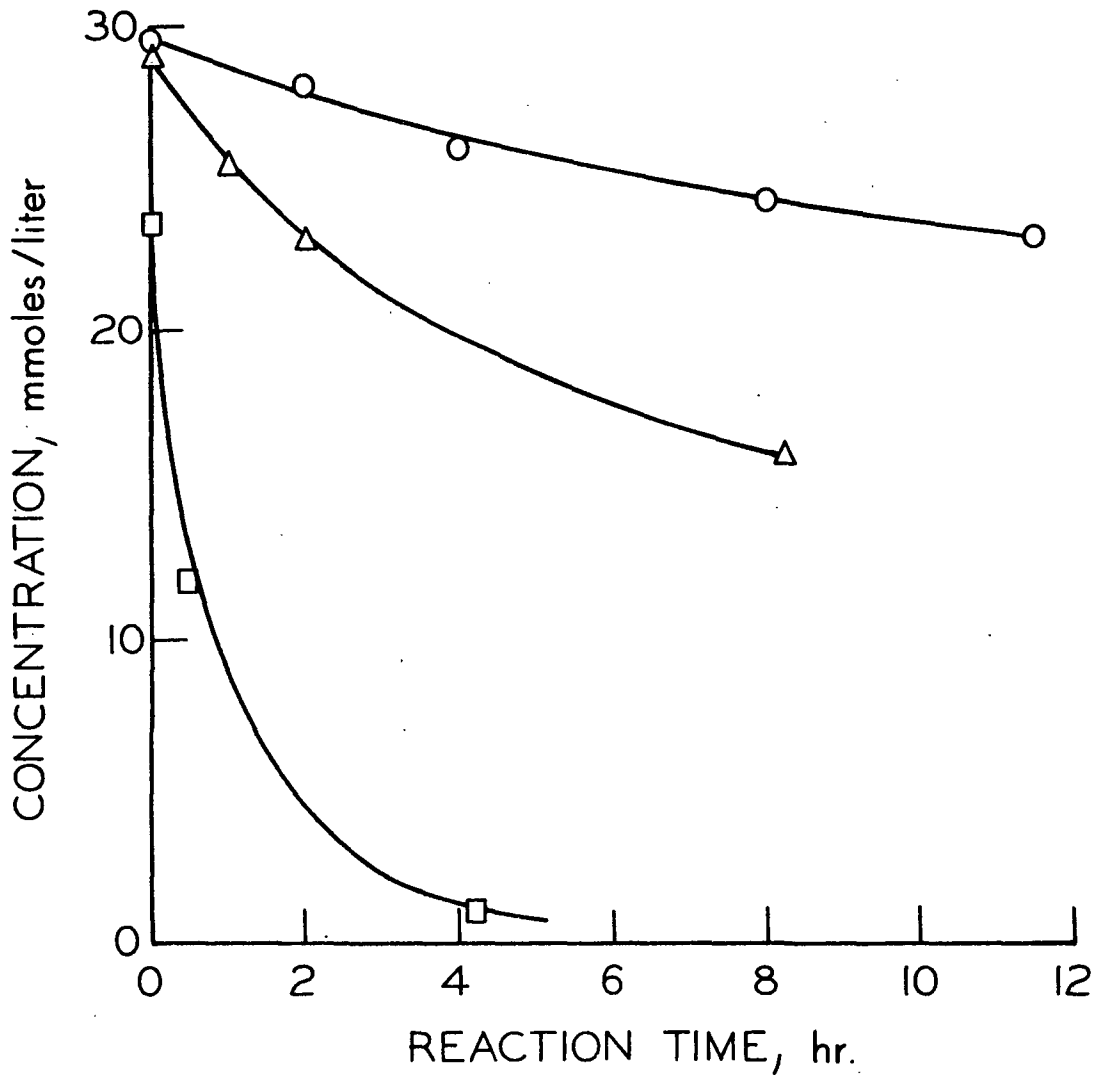


Figure 16. Degradation of Methyl β-D-Glucopyranoside (O), 1,5-Anhydrocellobiitol (Δ), and Cellobiitol (□), in 1.25N Sodium Hydroxide Containing Oxygen at 120°C. Initial Oxygen Pressure: 74.5 p.s.i.a. at 25°C.

The very rapid attainment of maximum peroxide concentrations compared to the relatively small loss of substrate at corresponding times suggests that the peroxides are formed primarily from oxidation of the substrates themselves, rather than from secondary oxidations of products. Furthermore, the maximum concentrations of peroxides are roughly proportional to the number of hydroxyl groups on the carbohydrate molecules: Cellobiitol > 1,5-anhydrocellobiitol > methyl β-D-glucoside, each having 9, 7, and 4 hydroxyl groups, respectively.

The very rapid decrease of peroxides in the case of cellobiitol is probably due to the very rapid rate of reaction of the model, which, in turn, is most likely caused by a rapid, nonoxidative decomposition. Cellobiitol is very much more reactive than methyl β-D-glucoside in oxygen-free alkaline solutions (38), presumably because the flexibility of the glucitol chain permits nucleophilic displacement at the C^4 atom by the C1 hydroxyl (alkoxide ion in basic solution). Consequently, the substrate is being degraded rapidly by a competing pathway, and less is available for the oxidative route in which peroxides are formed.

The observations made in investigating peroxide formation lead to questions regarding the nature of the peroxidic species and their role in the degradation reactions. Unfortunately, no satisfactory answers are available yet.

BOUND METHANOL

Under all conditions used in this investigation, the rate of formation of methanol from methyl β-D-glucoside was found to be always less than the rate of degradation of the glucoside. Consequently, less than one mole of methanol was generated from each mole of glucoside that disappeared. The same phenomenon was observed with methyl β-D-xyloside and methyl 6-deoxy β-D-glucoside (see Fig. 10). On the other hand, a mole equivalent of methanol is released from methyl

2-deoxy β-D-glucoside. The difference between the reaction of methyl β-D-glucoside and its 2-deoxy analog is illustrated in Fig. 17.

That methanol is not oxidized in the system is evident from direct investigations of the stability of methanol, and is substantiated by the fact that all the methanol is recovered in the degradation of methyl 2-deoxy β-D-glucoside. The methanol which is not detected as methanol or unreacted methyl β-D-glucoside must, therefore, be bound to some degradation product. This hypothesis was confirmed by hydrolyzing a reaction sample (as described in Appendix III) and measuring the methanol liberated. The results are given in Table VI.

TABLE VI

EVIDENCE FOR THE EXISTENCE OF BOUND METHANOL

		Concn., mmole/liter
Glucoside Present Initially		10.00
After reaction[a]		7.73
Glucoside degraded		2.27
Methanol liberated		
During reaction		1.34
During acid hydrolysis		8.80
Total		10.14
Bound methanol[b]	Method (1)	0.93
	Method (2)	1.07

[a] 142 hr. at 99°C.; 1.25N NaOH; 74.5 p.s.i.a. O_2.

[b] Method
(1) Difference between glucoside degraded and methanol liberated during reaction.
(2) Difference between methanol liberated during acid hydrolysis and glucoside present after reaction.

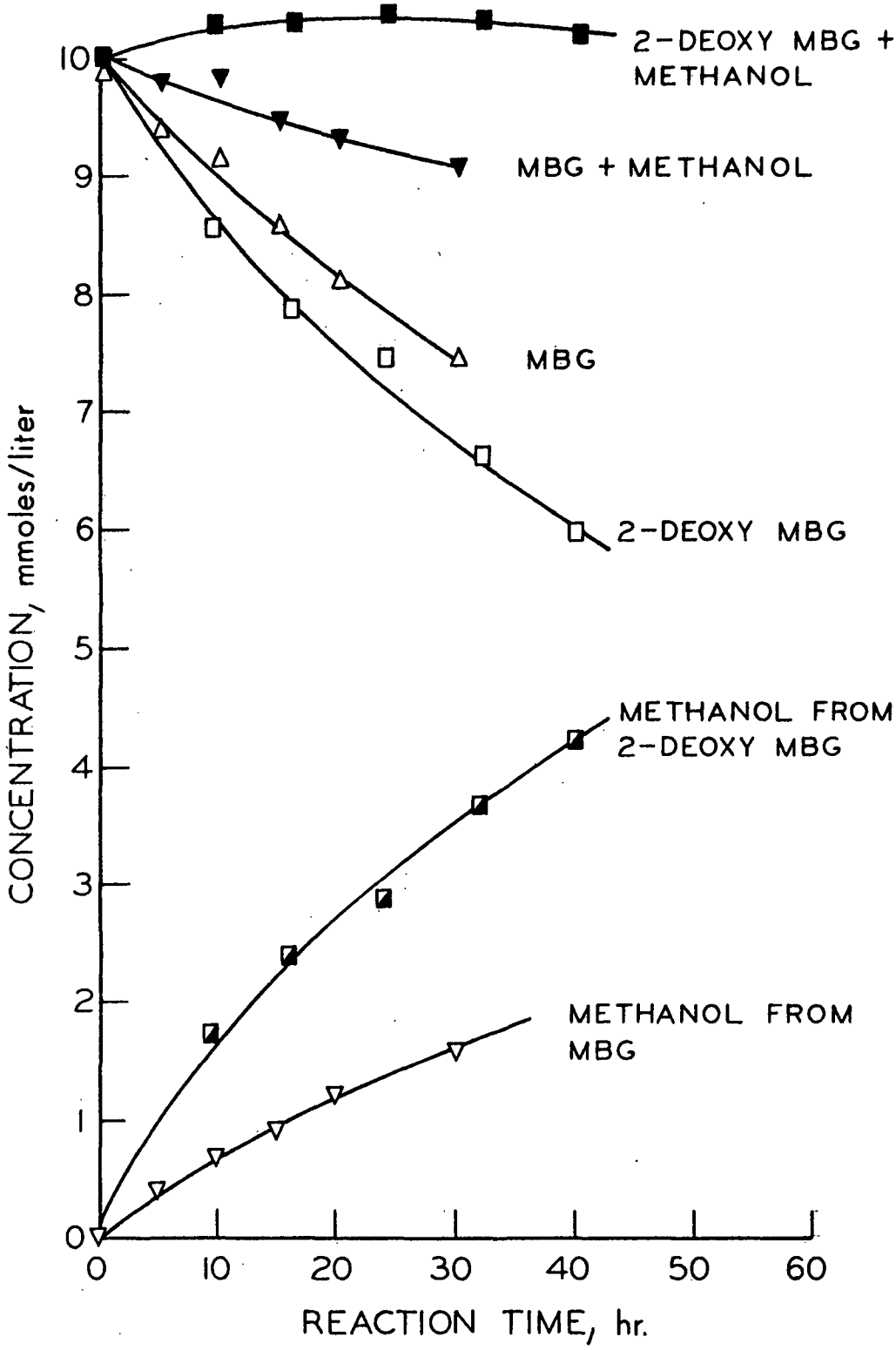
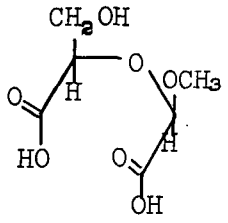
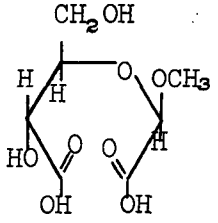


Figure 17. Unreacted Glucoside and Methanol Formed in Degradations of Methyl β-D-Glucoside and 2-Deoxy Methyl β-D-Glucoside in 1.25N Sodium Hydroxide at 120°C. with Initial Oxygen Pressure of 74.5 p.s.i.a. at 25°C.

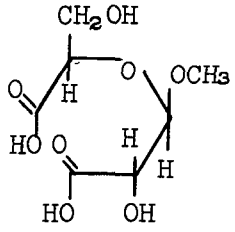
Possible products which might account for the bound methanol were considered. The oxidized glucosides such as L'-methoxy-D-hydroxy-methyl diglycolic acid (I) or the similar dibasic acids (II) and (III) resulting from oxidative cleavage of the pyran ring are likely candidates. The corresponding acids with C6 carboxyl groups are also possible.



I

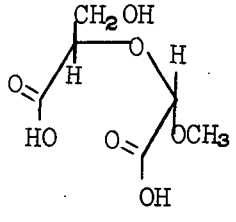


II



III

D'-Methoxy-D-hydroxymethyl diglycolic acid (IV) has been identified as a product of the air oxidation of methyl α-D-glucopyranoside in cuprammonium solution (39), consequently this author thought it likely that the similar compound (I) might be formed from the oxygen oxidation of the β-glucoside in sodium hydroxide solution.



IV

The stability of the suspected product was estimated by using the strontium salt of (IV) which was available. The results are shown in Table VII, and show that the dibasic acid (IV) is less reactive than methyl β-D-glucoside by a factor of at least ten. It should be noted that (IV) differs from (I) only in

its configuration about the acetal function. This difference would not be expected to have a large effect on the reactivity of the compound. Thus, an acid like (I) should be stable enough to explain the phenomenon of bound methanol.

TABLE VII

STABILITY OF D'-METHOXY-D-HYDROXYMETHYL DIGLYCOLIC ACID RELATIVE TO METHYL β-D-GLUCOPYRANOSIDE

Reaction Time, hr.	Dibasic Acid[a] $\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$	Methyl β-D-Glucoside Glucoside Reacted[b]	Methyl β-D-Glucoside $\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$
4.5	0.0058	0.05	0.032
29.0	0.0167	0.255	0.160

[a] D'-Methoxy-D-hydroxymethyl diglycolic acid (IV).

[b] Expressed as mole fraction.

The reason why bound methanol is not observed with the 2-deoxy glucoside is unknown.

ACIDIC REACTION PRODUCTS

It was beyond the scope of the present investigation to perform a detailed product analysis. However, several acidic products were detected by gas-liquid chromatography, and attempts were made to identify them. Gas chromatographic retention times of a number of known compounds were determined in order to establish a rough correlation between molecular structure and retention time. These are given in Appendix IV.

Three of the known acids examined had retention times similar to those of the acidic products (see Fig. 18). Arabinonic acid is a likely product. It is

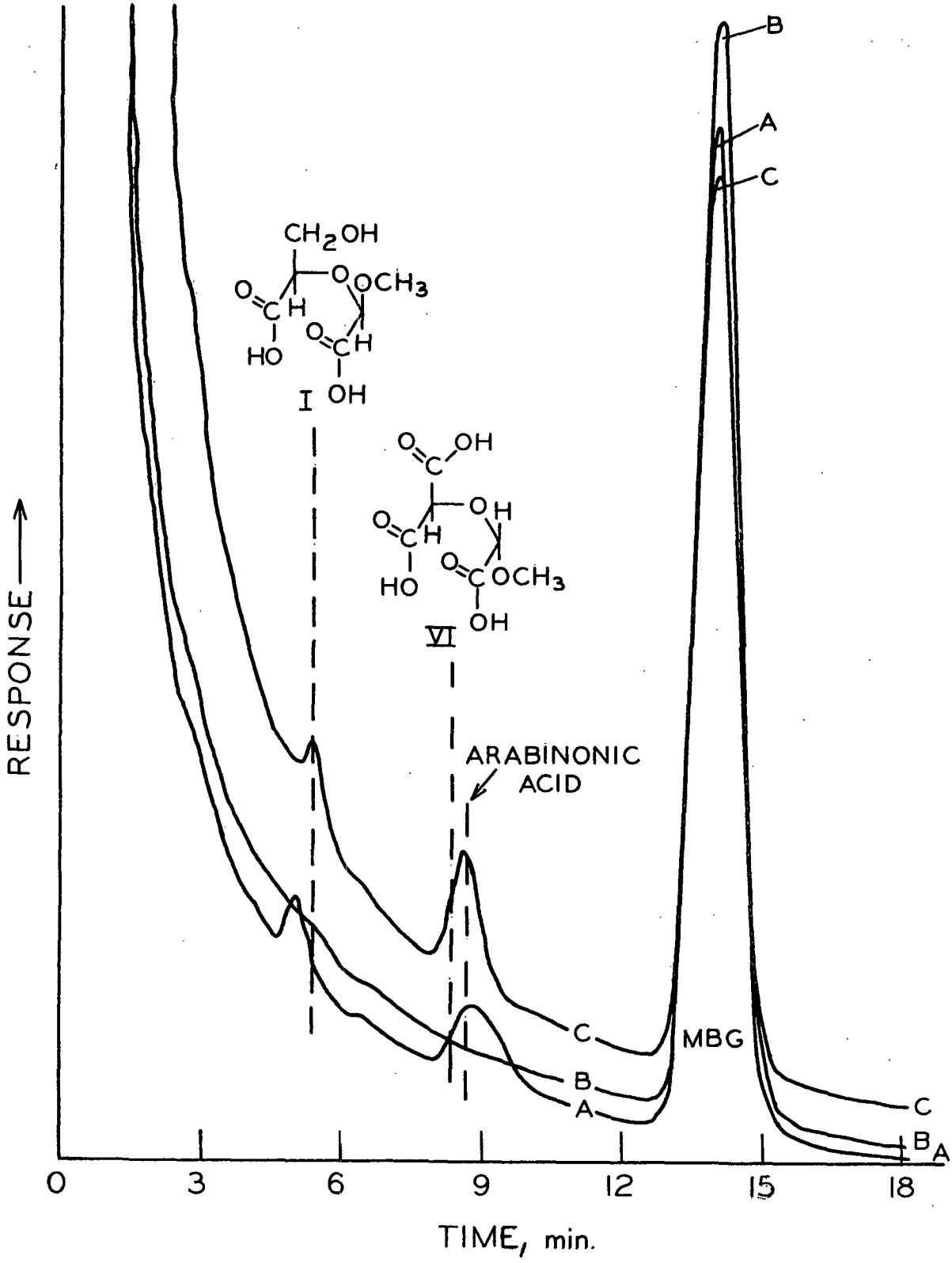
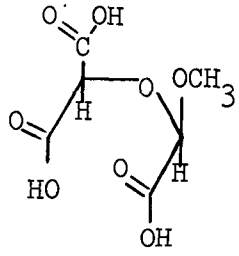
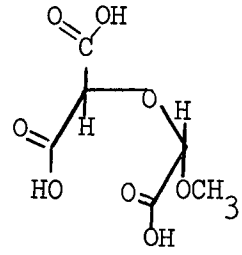


Figure 18. Products of Methyl β-D-Glucopyranoside Oxidation Detected by Gas Chromatography. A: Acidic and Neutral; B: Neutral; C: Neutral with Acids I and II and Arabinonic Acid Added. Run as TMS Derivatives

questionable whether L'-methoxy-D-hydroxymethyl diglycolic acid (I) is present. A small amount of the tribasic acid (V)



V



VI

(L'-methoxy-D-carboxymethyl diglycolic acid) might be produced during reaction, but not in sufficient quantity to account for all the "bound" methanol. A sample of this particular acid was not available for testing, but based on the relative retention times of the dibasic acids (I and IV) (0.43 and 0.40, respectively, relative to MBG) and the retention time of the tribasic acid (VI) which was available, (V) would be expected to have a retention time of about 9.1 minutes. Thus, it would fall where the shoulder is seen on the intermediate peak of Curve A. If it is present, its concentration must be very low, unless the quantitative analysis is in error. The method used required the conversion of the acid to its trimethylsilyl ester, but the extent of conversion to the derivative, its stability and its response to the hydrogen flame detector have not been determined.

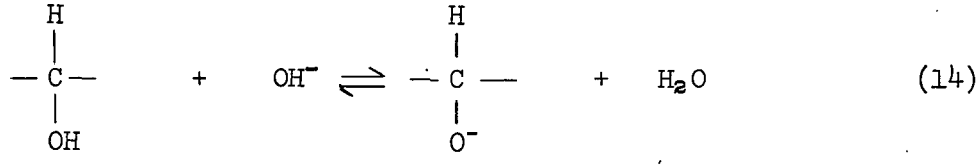
It is interesting to note that the acidic product peaks are not present in chromatograms of similar reaction solutions run in unlined, stainless steel reactors. Suitable control reactions run in the lined reactors ruled out the possibility of the peaks being artifacts caused by the linings.

DISCUSSION OF REACTION MECHANISM

The experimental results of this investigation provide important clues regarding certain aspects of the oxidation of methyl β-D-glucoside in alkaline solutions and leave little doubt that the mechanism is complex. The degradative reactions of cellulose during oxygen bleaching are most certainly even more complex because of the influence of the additional components present in the pulp. The following discussion will consider the mechanistic implications of the model study results, and their extension to the oxygen bleaching system.

Formation of Carbinolate Ion

The initial step in the reaction sequence must be the formation of a carbinolate ion as shown in (14). The lack of reactivity of the glucoside



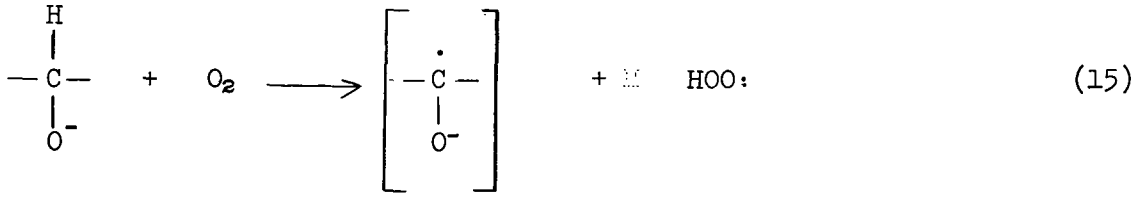
(14)

when all hydroxyls are blocked and, thereby, prevented from forming the carbinolate ion, and the direct relation between the number of free hydroxyls and reactivity are interpreted as evidence in support of this step. The location of the carbinolate ion is probably of little importance to subsequent oxidation, but the ease of forming the carbinolate ion would depend on its location. Theoretical considerations of the glucopyranose ring structure suggest that the ease of ionization would follow the order: C2 > C3 ≃ C4 > C6 (40). Oxidation, therefore, would be expected to follow the same order, with the C6 position being the most difficult to oxidize.

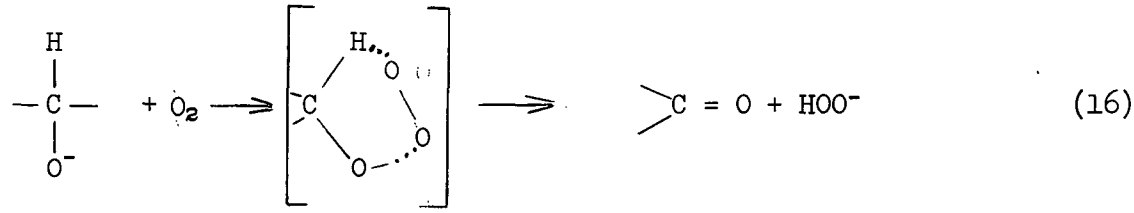
The carbinolate ion would provide increased electron density and facilitate removal of the attached hydrogen.

Direct Attack by Oxygen

Oxidation must begin with a direct interaction of the carbinolate groups with oxygen, because induction periods are not observed. Also, there is no evidence for autocatalysis. The initial oxidation may involve either homolytic or heterolytic cleavage of the carbon-hydrogen bond as shown by Steps (15) and (16), respectively. Both pathways result in the formation of peroxidic species which would be expected to react with the glucoside and cause autocatalysis.



(15)



(16)

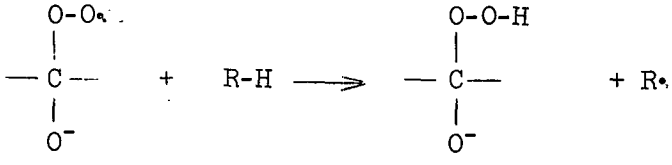
However, in these studies where the concentration of glucoside was low, the peroxidic species may decompose by reaction with water, alkali, or glucoside degradation products before they can react with glucoside molecules. Therefore, very little, if any, autocatalysis would be detectable.

The keto glucoside that would be formed by Step (16) might be expected to undergo rapid elimination of its methyl aglucone by a β-alkoxy carbonyl elimination. If this were so it would be difficult to explain the origin of the bound methanol by the scheme represented in (16). However, the oxidation of keto glucosides in alkaline solutions with oxygen does not seem to have been investigated, and it is possible that the keto glucoside might be oxidized at a rate which can compete with the base-catalyzed elimination rate.

Peroxide Formation

The origin of the peroxides which were experimentally measured is uncertain. Direct oxidation of carbinolate groups would result in the formation of perhydroxyl radicals [Equation (15)] or hydroperoxyl anions [Equation (16)]. However, these species would most likely react further to form other peroxides or decomposition products. Hydrogen peroxide was found to degrade very rapidly under the experimental conditions employed in this work. It is, therefore, unlikely that hydrogen peroxide comprised the measured peroxides. Hydroperoxides might be easily formed through Steps (17) and (18) from the radical generated in (15). Step 18 represents the abstraction of a labile hydrogen and may be intramolecular as well as intermolecular because of the multiple hydrogen

(17)



(18)

atoms that can be abstracted from the glucoside molecule. It is doubtful, however, that the hydroperoxide would be stable in the alkaline solution. Few stable hydroperoxides can be formed in an excess of strong base (41). Hence, more stable organic peroxides are probably formed in subsequent rapid reactions that are yet undefined.

Secondary Reactions

Incomplete liberation of methanol from the degraded glucoside is evidence that the glucosidic bond is not cleaved immediately upon oxidation of the

glucoside. The reaction mechanism, therefore, is not as simple as Brooks (23) pictured it. In nearly all reactions methanol liberation accompanied glucoside degradation, and about fifty or sixty percent of the possible methanol was released at a given reaction time. Induction periods were not observed. Hence, the oxidation and glucosidic bond cleavage reactions do not seem to be entirely independent. Perhaps the initial oxidation products degrade through intramolecular reactions which result with about equal ease in either glucosidic bond cleavage (and free methanol) or products to which methanol is still attached. The "bound methanol product" might slowly liberate methanol in a subsequent step.

Other secondary reactions of the oxidized glucoside probably lead to a complex mixture of products. Solutions resulting from the action of air and alkali on sugars were called "horrible" mixtures by Nef (42) long ago.

Significance of Kinetic Order

The rate of disappearance of glucoside can best be approximated, at least during the initial stages of reaction, by the expression

$$-d\,[G]/dt = k[G]^2\,[O_2]\,[NaOH] \qquad (19)$$

where the terms in brackets represent the concentrations of glucoside, oxygen and sodium hydroxide, respectively. A first-order dependence on hydroxide is assumed in this discussion, though a possible variable dependence may exist as was discussed earlier.

Equation (19) suggests an overall reaction order of four, and immediately points to a complex mechanism. The second-order dependence on glucoside is especially intriguing, but at present it has no satisfactory explanation.

Numerous hypothetical mechanisms were considered in seeking an explanation, but none fits the experimentally determined rate expression.

A 1.5-order dependence on glucoside would be anticipated if the reaction were a nonautocatalytic, free-radical chain autoxidation initiated directly by oxygen. The autoxidations of glucose in aqueous solution (43) and methyl β-D-glucoside in the melt (44) appear to be such reactions. By analogy, the oxidation of methyl β-D-glucoside in alkaline solution might be expected to be similar.

The following hypothetical reaction scheme illustrates how a 1.5-order dependence on glucoside might arise. $H\text{-}\overset{|}{C}\text{-}OH$ represents an active carbinol group.

$$H\text{-}\overset{|}{C}\text{-}OH + OH^- \overset{K}{\rightleftharpoons} H\text{-}\overset{|}{C}\text{-}O^- + H_2O \qquad (20)$$

$$H\text{-}\overset{|}{C}\text{-}O^- + O_2 \xrightarrow{k_1} \cdot\overset{|}{C}\text{-}O^- + HOO\cdot \qquad (21)$$

$$\cdot\overset{|}{C}\text{-}O^- + O_2 \xrightarrow{k_2} \cdot O\text{-}O\text{-}\overset{|}{C}\text{-}O^- \qquad (22)$$

$$\cdot OO\text{-}\overset{|}{C}\text{-}O^- + H\text{-}\overset{|}{C}\text{-}O^- \xrightarrow{k_3} HOO\text{-}\overset{|}{C}\text{-}O^- + \cdot\overset{|}{C}\text{-}O^- \qquad (23)$$

$$2(\cdot OO\text{-}\overset{|}{C}\text{-}O^-) \xrightarrow{k_4} \text{inactive products} \qquad (24)$$

$$2(\cdot\overset{|}{C}\text{-}O^-) \xrightarrow{k_5} \text{inactive products} \qquad (25)$$

$$\cdot\overset{|}{C}\text{-}O^- + \cdot OO\text{-}\overset{|}{C}\text{-}O^- \xrightarrow{k_6} \text{inactive products} \qquad (26)$$

If it is assumed that Step (22) is very fast, then with a large excess of oxygen present, it is unlikely that Steps (25) and (26) are important. Termination of the radical chain would occur primarily by Step (24). With this assumption and by applying the usual steady state assumption to radicals (45),

the above mechanism leads to the following rate expression (for long chains)

$$\text{rate} = (k_1/k_4)^{0.5}\, k_3 K^{1.5}\, [G]^{1.5}\, [O_2]^{0.5}\, [OH^-]^{1.5} \qquad (27)$$

$$\text{or rate} \propto [G]^{1.5}\, [O_2]^{0.5}\, [OH^-]^{1.5} \qquad (28).$$

It is noted that this treatment predicts a 1.5-order dependence on glucoside. Also, all the orders with respect to the reactants are different from those found experimentally [Equation (19)]. Therefore, the particular example illustrated obviously does not fit the experimental results. The introduction of alternate steps into the reaction sequence, or the variation of assumptions made in deriving the rate equation, results in more complex rate expressions, none of which predicts greater than 1.5-order dependencies on glucoside. If it is assumed that the order is really 1.5, very large experimental errors (of the order of 75%) would be necessary in order to account for the observed second-order dependence. Such errors cannot be justified.

A more plausible rationalization of the second-order dependence relates to the method of determining it. As discussed previously, there are no fundamental objections to calculating orders by the differential method using initial rates. However, a complication might arise if the reaction is complex and a mechanism change occurs along with changes in initial reactant concentration. The change might involve the addition or substitution of a step in a multistep reaction, and need not be a complete change in mechanism. For example, if there were additional reaction steps that might take on importance at a higher reactant concentration, then the overall rate would be greater than anticipated. As a consequence, the order determined from a plot of the logarithm of initial rate against logarithm of initial concentration according to Equation (8) would be inflated.

$$\log v_i = \log k'' + a \log [G]_i \qquad (8).$$

However, if this were the case in the present investigation, then it is strange that the orders came out to be so close to integral values. It would seem unlikely that the results were fortuitous.

Competing Reactions

The discussion up to this point has been concerned with the reaction of the model glucoside with oxygen and alkali. The complexity of the reaction is apparent. The effect of added glucose and hydroquinone suggest an even more complicated reaction in their presence. Although this is of minor importance to the glucoside reaction itself, it has significant implications with regard to the degradation of cellulose during oxygen bleaching. The large accelerating influence of hydroquinone and the smaller, but important, effect of glucose suggest that easily-oxidized components of pulp may contribute greatly to the overall degradation of the cellulose by producing reactive peroxidic species that can subsequently react with the cellulose. Considering the large amount of lignin, hemicelluloses, and reducing carbohydrate fragments present in pulp and their close contact with the cellulose chains, one might expect a major part of the cellulose degradation to result from attack by peroxides. This possibility leads to an explanation of the role of magnesium carbonate during oxygen bleaching and the reason why it has only a small influence on the reaction of methyl β-D-glucoside.

The Role of Magnesium Carbonate

The work of Samuelson and Stolpe (18) with cellobiitol led them to conclude that magnesium carbonate inhibits the degradation of cellulose by complexing with the peroxides formed during oxidation. The stabilizing influence of

magnesium on peroxides is well known. Magnesium ion stabilizes hydrogen peroxide under appropriate conditions (46). Also, very stable peroxide compounds have been formed by mixing basic magnesium carbonate and hydrogen peroxide solutions (47). Thus, there is little doubt that magnesium carbonate is capable of stabilizing peroxides formed during oxygen bleaching.

The effects of magnesium carbonate in the model system and during oxygen bleaching are consistent with the idea of complex formation. Oxidation of glucosides in the model system leads to formation of peroxides, but these apparently do not attack other glucoside molecules because autocatalytic effects are not observed. Hence, stabilization of the peroxides by magnesium carbonate would have little, if any, effect on the reaction. During oxygen bleaching, on the other hand, many competing reactions are possible. Peroxides could be readily generated from easily oxidized materials, e.g., compounds containing carbonyl groups. Because of the close proximity of the various pulp components, peroxides would not have far to travel before reacting with a cellulose chain. For this reason the effect of peroxides could be much more important during bleaching than in the model glucoside reactions. If this is true, deactivating the peroxides as they are produced would be expected to have a greater influence in the bleaching of pulp than in the model system.

CONCLUSIONS

Methyl β-D-glucopyranoside is oxidized in hot (100-120°C.), alkaline solutions containing molecular oxygen by a complex reaction mechanism. Oxidation of the glucoside and cleavage of the glucosidic bond to release methanol do not occur simultaneously. The liberation of methanol occurs at about one-half the rate of disappearance of the glucoside, and generally parallels the degradation. There are no signs of either induction periods or autocatalysis; slight indications of product inhibition were apparent at long reaction times.

Initial-rate kinetic studies suggested that the degradation reaction is approximately fourth-order overall; second-order in glucoside, first-order in oxygen and first-order (possibly variable) in sodium hydroxide. Possible reasons for the second-order dependence on glucoside were considered, but no satisfactory explanation yet exists. The apparent activation energy for the degradation reaction is 21 kcal./mole.

Reaction of model compounds having some blocked hydroxyl groups showed the need for free hydroxyl groups. Reaction rate roughly correlates with the number of free hydroxyl groups, suggesting that no single hydroxyl is sufficient to account for the overall reactivity of methyl β-D-glucoside. The C6 hydroxyl group seems to have little influence on the rate.

It is postulated that hydroxyl groups are ionized in the alkaline solution and that the oxygen cleaves the carbon-hydrogen bond of the carbinolate ion thus formed. It is not yet known whether homolytic or heterolytic cleavage occurs. The initial oxidation product subsequently breaks down to liberate methanol or to form a stable product or intermediate to which methanol is still attached.

Peroxides are generated during oxidation, but their nature and method of formation is unknown.

Additional reaction pathways appear to be available when certain additives are present. The addition of hydroquinone or glucose increases the reaction rate, probably through reactions between the glucoside and peroxides generated in the oxidation of the additives. These results suggest that, since relatively large amounts of easily oxidized components are present in pulps, the reaction of cellulose with peroxides may be a major degradative pathway during oxygen bleaching.

Magnesium carbonate has a small inhibitory effect on the degradation of the glucoside. The effect is not as large as would be anticipated from its effect on cellulose degradation during oxygen bleaching. The difference is possibly attributable to the various modes of formation and reaction of peroxides available during bleaching which are not possible in the model system. The magnesium carbonate is believed to stabilize peroxides through complex formation.

Reaction is faster in stainless-steel reactors than in teflon-lined vessels, and some acidic products appear to be degraded when metal is present. It is not known whether metal ions affect the bleaching reactions, but teflon-lined vessels such as the ones designed and used in this work could be employed to check the effect. Model studies, however, demand that inadvertent catalytic effects of metals be eliminated, which requires a reactor lined with inert material. The tube-type reactors used in the present investigation were satisfactory, but a more convenient system would facilitate future studies. An improved reaction vessel has been conceived, and is described in Appendix VII.

SUGGESTIONS FOR FUTURE RESEARCH

It is apparent from this study that much more research is needed to understand the alkaline oxidation reactions of carbohydrate material. Because of the current interest in oxygen bleaching, the investigations will be of industrial as well as academic importance. The effects of glucose and hydroquinone on the reaction of methyl β-D-glucoside suggest that the degradation of cellulose during oxygen bleaching is greatly affected by the presence of other components in the pulp. Studies of interactions between cellulose, hemicelluloses, and lignin would be very valuable. For a start these might be oriented toward elucidating the connection between the formation of peroxides from the various components and the rate of degradation of the cellulose. This might be done with pulps of different lignin and hemicellulose contents or with synthetic mixtures of model compounds. The results would help to determine whether the degradation of cellulose is caused primarily by direct oxidation by oxygen or from attack by peroxides formed in the oxidation of other substances. The addition of inhibitors, such as magnesium carbonate, would be of assistance if they actually exert their influence through complex formation with peroxides.

With regard to the cellulose model, methyl β-D-glucoside, much work remains to be done. A complete product analysis would be invaluable. The identification of the product to which methanol is bound would provide important clues as to the mechanism. Modern gas chromatographic methods and mass spectrometry would greatly simplify the analysis of a complex product mixture.

It would also be helpful to know the nature of the peroxides that were detected in the present work. However, this might be a difficult task because

analytic methods for peroxides are generally nonspecific, and are often interfered with by other materials. Yet it might be possible under certain conditions to stabilize the peroxides as they are formed, e.g., complex formation, so they could be isolated and identified by spectrophotometric means.

The second-order dependence on glucoside deserves further study, as does the variation in the dependence on alkali. A more complete study of the dependence on alkali and the possible existence of salt effects would demand two preliminary investigations; one to find a suitable salt to use in maintaining constant ionic strength and another to determine the relationship between dissolved oxygen, oxygen pressure, temperature, and solute concentration. The reactor described in Appendix VII could be employed in the latter study. After equilibrium conditions are established, the solution could be sampled easily. The dissolved oxygen could then be determined by conventional techniques.

The model studies should be extended to the disaccharides, such as methyl β-cellobioside or 1,5-anhydrocellobiitol, in order to ascertain the effect of the C4 linkage on the rate of degradation. Preliminary investigations with both compounds were made during the studies with methyl glucoside. Both produced the corresponding monosaccharides, methyl β-D-glucoside and 1,5-anhydroglucitol.

It would also be interesting to investigate the reaction of methyl 2-deoxy β-D-glucoside to determine why no bound methanol is produced.

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APPENDIX I

CONSTRUCTION OF LINED REACTORS

PRELIMINARY ATTEMPTS

Several reactors were designed and numerous attempts were made to line them before a satisfactory reactor was developed. All designs were of the pipe type with a valve at one end and sealed at the other. The first had threaded joints to connect the valve and sealing cap to the main body. Attempts to line it with Kel-F resin consisted of filling the assembled reactor with Kel-F Brand Plastic Dispersion Coating System (KX-631)*, and inverting the reactor to allow the excess coating to drain out. Complete removal of the solvents is necessary before the coating is fused, otherwise the expansion of the solvents on heating causes blistering. Several methods of removing the solvents from the reactor were tested, but none were successful. Consequently, all attempts to line the reactors in this way resulted in blistered linings.

Better results were obtained by lining the reactor components before assembling them. This method yielded satisfactory linings on the components, but no way was found to form reliable seals at the joints of the reactors. Flange joints offered an alternative solution to the problem of sealing the reactor and led to the successful design which developed into the reactors used. Figure 19 shows the component parts of the reactor. The assembled view is shown in Fig. 3 in the text.

*Product of the 3M Company, St. Paul, Minnesota.

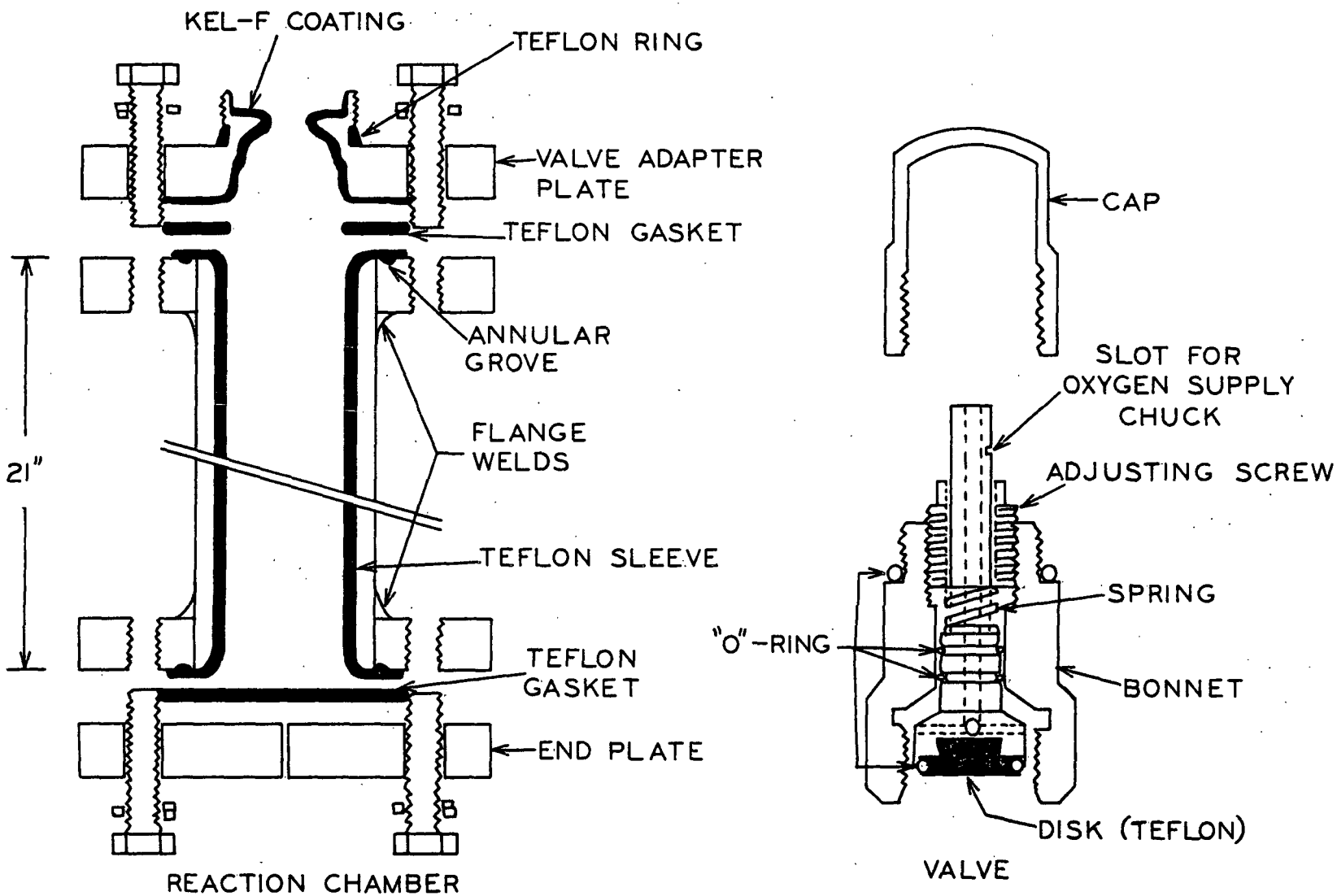


Figure 19. Reactor Components (Actual Size)

Three methods of lining the reaction chamber were tried. The first involved spray application of a teflon resin. Spraying, however, resulted in overspray and dust entrainment which caused pinholes to form in the films. The problems could not be overcome, and the method was discarded in favor of others.

The second method consisted of coating a film of Kel-F in the reaction chamber. Various casting techniques were tested, and the most successful was found to be a modified spin-casting process. The resin was poured onto the surface to completely coat it. The excess was allowed to run off, and the pipe section was spun in a lathe at about 600 r.p.m. The spinning helped to distribute the resin uniformly over the surface and eliminated problems of streaking often encountered with other techniques as the solvent evaporated. Heating the spinning pipe to about 60 °C. by placing an electric heat gun on the outer surface helped speed the removal of the solvents. When the film was set, the reactor was clamped in the vertical position at room temperature until the solvents had escaped. The film was then fused in a 480 °F.-oven for twenty minutes. Additional coats were applied in the same way until the desired film thickness was reached. The final coating was fused for 5 or 6 hours; then quenched in cold water. The method yielded pinhole free films, but required about three days of work. Replacement of linings was difficult.

A much simpler means of lining the reaction chambers was developed using sleeves of flexible, thin-walled teflon tubing. The method was quick, and replacement of sleeves was simple. The technique employed to insert the sleeves is described in the following paragraphs.

CONSTRUCTION OF REACTION CHAMBER

The metal part of the reaction chamber was constructed from a 21-inch long piece of Type 316 stainless steel seamless pipe (1 inch I.D.) to which steel flanges were welded. Seamless pipe was chosen for its smooth inner surface. Stainless steel was used, because it was found to impart a bright yellow green coloration to reaction solutions if breaks occurred in the lining and the solution contacted the metal. If solutions were colored, it was immediately apparent that the lining had failed.

The faces of the flanges were machined smooth and flush with the ends of the pipe. An annular groove was cut in the flange so that the pressure applied by the flange bolts would mold a ring on the flared end of the teflon sleeve and assist in locking the sleeve in place. The inner edges of the pipe ends were well rounded to minimize stress concentrations on the teflon sleeve.

INSERTING THE TEFLON SLEEVE

A piece of teflon tubing (1 inch O.D. with 0.05 inch wall thickness and about 23 inches long) was shrunk in the radial direction by manually and repeatedly forcing it through a series of smaller holes until it slipped easily into the pipe. Holes drilled in a piece of one-inch thick, polyvinyl chloride plastic plate were found to be satisfactory. The reaction chamber with the piece of tubing inside was heated at about 100°C. until the teflon expanded to form a snug fit (about one hour). After cooling, the extra teflon was cut off leaving 7/16 inch extended from each end of the pipe.

Each end of the tubing was flared by heating the teflon just to the melting point and rapidly shaping the end. Heating was done with a soft acetylene flame

aimed at the inner surface of the tubing starting about one-half inch in from the end and slowly moving out while the pipe was supported in a lathe and was being rotated slowly (about 50 r.p.m.). As soon as the entire end of the tubing became transparent, rotation was stopped and the flaring tool, which was held in the lathe tail stock, was carefully forced against the tubing, and held in place for a few minutes. The flaring tool was made from a piece of brass shaped to match the configuration of the pipe end with clearance allowances. Best results were obtained when it was not heated.

The flare was not formed in the conventional manner. Instead the outer edge of the tubing retained its original shape, but the rest of the heated portion of the teflon bulged and buckled to create a single fold with the outer edge of the tubing folded in toward the center.

LINING THE VALVE ADAPTER

The valve adapter was constructed from a modified valve seat of a McCanno-flo F602 ball valve welded to a steel flange. After smoothing the flange face and removing sharp angles, the surface to be lined was prepared by sandblasting, washing in carbon tetrachloride, and prebaking at 520°C. overnight.

Kel-F Brand Plastic Dispersion Coating System (KX-631)* was used to coat the surfaces. It was applied by pouring onto the surface the minimum amount required to give complete coverage. After rotating and tipping so that the resin flowed over the whole surface, the piece was spun in a lathe at 600 r.p.m. While spinning, the excess resin was removed from the valve seat with a spatula.

*Product of the 3M Company, St. Paul, Minnesota.

Spinning was continued until enough solvent had evaporated so that the surface was white. After at least an additional half hour drying at room temperature, the resin was partially cured by heating for 20 minutes in a 480°F. oven. The piece was cooled, and additional coats of resin were deposited in the same manner until a total film thickness of about 0.015 inch was obtained. The final coat was baked for about 5 hours at 480°C., then quenched in cold water.

VALVES

Originally, McCanno-flo F602 stainless steel ball valves with teflon-coated balls and teflon seats were to be used. However, the creep of the teflon under pressure caused the valves to develop leaks after a few heating cycles. The problem could not be solved with these valves. No other commercially available valve could be found to meet the requirements, so the special valve shown in Fig. 19 was designed. The important features of the valves are described in the text accompanying Fig. 3.

COMMENTS ON ASSEMBLING THE REACTORS

Six 1/4-inch machine bolts were used to bolt the flanges together at each end of the reactor. Ordinary lock washers on each bolt were found to provide sufficient spring tension to prevent leakage at the flanges during the rapid cooling periods encountered in use. Minimum sealing pressure was applied to the flange bolts in order to minimize flow, or "creep," in the teflon.

A small hole (1/64 inch) drilled through the end plate provided a vent which relieved pressure buildup between the gasket and the metal plate. Without the hole, excessive pressure built up between the gasket and the plate and caused the gasket to bulge and eventually rupture.

TESTING REACTORS FOR LINING BREAKS

The assembled reactors were checked for breaks in the linings using a dielectric test. Each reactor was filled with a dilute solution of sodium hydroxide and the resistance across the film was measured with a 500 volt d.c. potential applied through probes to the solution and the outside of the reactor. Resistances of less than 1000 megaohms were indicative of small breaks.

In addition to the dielectric test, the design of the reactors permitted visual inspection of the entire internal surface when the valve was removed. A grain-of-wheat light bulb suspended inside the reactor provided the necessary light.

APPENDIX II

MATERIALS

ORGANIC REACTANTS

Melting points correspond to corrected values, and were determined with a Thomas-Hoover Unimelt apparatus.

Optical rotations were made on a Zeiss-Winkel polarimeter.

METHYL β-D-GLUCOPYRANOSIDE

Methyl β-D-glucopyranoside was obtained from E. V. Best. It was purified by refluxing with 1N sodium hydroxide to remove reducing sugars, deionized, and recrystallized from ethanol (3X). The product had m.p. = 109-111°C., softened at 105°C.; $[\alpha]_D^{21}$ = -33.7° (H_2O, c = 2.0), calculated as hemihydrate. Literature values for the melting point range from 104 to 111°C. and specific rotations vary from -31.4 to 34.2 (48). The spread in values is probably due to variations in the amount of hemihydrate present.

The purity of the material was assayed by both paper chromatography and gas-liquid chromatography. Less than 0.1% glucose was present. No other impurities were detected.

METHYL 2-DEOXY β-D-ARABINO-HEXOPYRANOSIDE

Methyl 2-deoxy β-D-arabino-hexopyranoside (methyl 2-deoxy β-D-glucoside) was synthesized from 2-deoxy glucose through the tri-O-benzoyl-bromo-derivative as described in the next section.

Tetra-O-Benzoyl 2-Deoxy Glucose

Tetra-O-benzoyl 2-deoxy glucose was prepared from 2-deoxy glucose (Pfanstiehl Laboratories) by a modification of the procedure of Bergmann and coworkers (49). Finely powdered 2-deoxy glucose (15 g.) was suspended in dry pyridine (44.4 ml.). With stirring and cooling in an ice bath, benzoyl chloride (53.6 ml.) was added at the rate of about 2 ml./min. A white solid began to form after the addition of about one-third of the benzoyl chloride. Dry chloroform (50 ml.) was added to dissolve the solid. An additional 50-ml. portion of chloroform was added when more solid material formed after the addition of about two-thirds of the benzoyl chloride. After stirring the solution for 24 hr., water (4 ml.) was added to hydrolyze the excess benzoyl chloride. The solution was extracted with chloroform (350 ml.), and the chloroform extract was washed in sequence with 1N hydrochloric acid (3 x 700 ml.), saturated solution of sodium bicarbonate (3 x 200 ml.) and water. After drying over calcium chloride, it was concentrated to a thick sirup (62.5 g.), which was brominated without further purification.

Tri-O-Benzoyl 2-Deoxy-D-Glucosyl Bromide

The bromination procedure of Ness, et al. (50) as modified by Hultman (51) was adapted for this preparation.

Dichloroethane (49 ml.) and 32% hydrogen bromide in glacial acetic acid (46 ml.) were added to the sirupy tetra-O-benzoyl 2-deoxy glucose. The entire mass solidified within 5 min., so more dichloroethane (125 ml.) was added, and the solution was stirred for one hour. Chloroform (100 ml.) was added and the mixture was poured into ice water (500 ml.). The layers were separated, and the aqueous layer was washed with chloroform (100 ml.). The combined chloroform solutions were washed with ice water (2 x 400 ml.), dried over

$CaCl_2$, and concentrated at reduced pressure to a sirup. Crystals formed after dissolving the sirup in chloroform (200 ml.) and adding petroleum ether (30-60°C.) until turbidity persisted. After refrigerating overnight, the crystals were collected and recrystallized from chloroform (100 ml.) and petroleum ether (150 ml.). Yield was 18 g. of white needle crystals melting sharply at 135°C. Literature m.p. 139°C. (52). An additional 21 g. of crystals were recovered from the mother liquor.

Methyl tri-O-Benzoyl 2-Deoxy β-D-Glucopyranoside

The procedure of Schroeder and Green (53) for the Koenigs-Knorr synthesis of alkyl glucosides was used. Drierite (10-20 mesh, 24 g.), yellow mercuric oxide (7.8 g.), mercuric bromide (0.6 g.), purified chloroform (120 ml.), and anhydrous methanol (120 ml.) were stirred in a stoppered flask for 0.5 hr. The tri-O-benzoyl 2-deoxy glucosyl bromide (18 g., first crop) was added and stirred for 7.5 hr. The salts were removed, and the solution was concentrated to a sirup. The product was crystallized from methanol. Yield was 12.0 g. (first crop). M.p. = 88-90.5°C. Literature: 88°C. (52).

Methyl 2-Deoxy β-D-Glucopyranoside

The tri-O-benzoyl derivative (12 g.) was debenzoylated with sodium methoxide (3 ml. of 1N) in chloroform:methanol (1/2:v/v) solution (90 ml.). Debenzoylation was complete within 23 hr. at 25°C. The solution was extracted with water (3 x 20 ml.). The combined aqueous layers were extracted with chloroform (25 ml.), and concentrated at reduced pressure to about 30 ml. Two grams of sodium hydroxide in 50 ml. of water were added, and the solution was heated to boiling. After cooling and sitting overnight, the solution was deionized and concentrated to a thick sirup, which was crystallized from acetone. Yield was 1.35 g. (first crop). Recrystallization from ethyl

acetate yielded 1.06 g., m.p., 120-121.5°C., $[\alpha]_D^{21}$ = -46.0° (H_2O, c = 1). Literature: m.p. 121-122°C. (54), 122°C. (55), 122-123°C. (56); $[\alpha]_D$ = -43.4° (H_2O, c = 1.0) (54), -45 (H_2O, c= 1.0) (55), -48 (H_2O) (56).

METHYL 6-DEOXY β-D-GLUCOPYRANOSIDE

Methyl 6-deoxy β-D-glucopyranoside was purchased from the Pierce Chemical Company (Rockford, Illinois). No impurities were detected by gas chromatography. M.p., 131-132°C.; $[\alpha]_D^{20}$ = -56.1° (H_2O, c = 1.0). Literature (57): m.p., 131-132°C.; $[\alpha]_D^{20}$ = -55.3° (H_2O, c = 9).

METHYL β-D-XYLOPYRANOSIDE

Methyl β-D-xylopyranoside was obtained from Pfanstiehl Chemical Company (Milwaukee, Wisconsin). No impurities were detected by gas chromatography. M.p., 156.7°C.; $[\alpha]_D^{21}$ = -64.4° (H_2O, c = 1.0). Literature: m.p., 156-157°C. (58); $[\alpha]_D^{20}$ = -65.8° (H_2O, c = 9) (58) and -65.3° (59).

METHYL TETRA-O-METHYL β-D-GLUCOPYRANOSIDE

A sample of this compound, prepared by D. P. Hultman (60), was used without further purification. M.p., 37.5-39°C.; $[\alpha]_D^{25}$ = -19.4° (H_2O, c = 1.0). Literature (61): m.p. = 40-41°C., $[\alpha]_D^{25}$ = -17° (H_2O, c = 4).

METHYL 3,4,6-TRI-O-METHYL β-D-GLUCOPYRANOSIDE

This compound was prepared by D. P. Hultman (60), and had been recrystallized from hexane to a constant melting point. M.p., 51.5-52.0°C.; $[\alpha]_D^{22}$ = -17.1 ($CHCl_3$, c = 1.4). Literature (62): m.p. 51.5-52.5°C.; $[\alpha]_D^{25}$ = -16.4° ($CHCl_3$, c = 2).

METHYL 3-O-METHYL (α,β)-D-GLUCOPYRANOSIDE

A sample of methyl 3-O-methyl glucoside sirup was obtained from Dr. N. S. Thompson. It was found to be a pure mixture of the α- and β-anomers. Its gas chromatographic retention time (run as TMS derivative) was the same as a mixture of α- and β-glucoside prepared by treating 3-O-methyl glucose with methanol and HCl. Upon acid hydrolysis, it yielded two products whose retention times were identical to those of the anomers of 3-O-methyl glucose. The original sirup gave a negative Fehling's test. $[\alpha]_D^{21}$ = +99.3° (H_2O, c = 5.82). Literature, $[\alpha]_D$:

α-anomer, +164 ± 2° (H_2O, c = 0.86) (63),

β-anomer, -26.6° (H_2O, c = 5.5) (64); -25.3° (H_2O, c = 1.59) (65); -27° (H_2O) (66).

From the known specific rotations of the mixture and the pure anomers, the composition of the 3-O-methyl glucoside preparation was calculated to be 47% β and 53% α.

CELLOBIITOL

Cellobiitol monohydrate was recovered from crude cellobiitol by recrystallization from methanol and ethanol according to the method of Wolfrom and Fields (67). The crystalline product melted at 104-105.5°C.; $[\alpha]_D^{20}$ = -7.24° (H_2O, c = 6). Literature (67): m.p., 106-106.5°C.; $[\alpha]_D$ = -7.8 (H_2O).

1,5-ANHYDROCELLOBIITOL

A sample of 1,5-anhydrocellobiitol heptaacetate from Dr. L. R. Schroeder was deacetylated with sodium methoxide in methanol and heated with 1N sodium

hydroxide in order to remove reducing sugars. The solution was decolorized with charcoal, deionized and concentrated to dryness at reduced pressure. Multiple additions of absolute ethanol and repeated evacuations were used to remove final traces of water. The white crystalline product was recrystallized from hot, absolute ethanol to which about 6% water was added. Crystals formed as the solution cooled gradually to room temperature. Product melted at 204.5-205.5°C.; $[\alpha]_D^{31}$ = +29.4° (H_2O, c = 2.84). Literature (68): m.p., 172°C.; $[\alpha]_D$ = +29.3 (H_2O, c = 4.64).

Gas chromatography of the sample showed only a single peak with the same retention time as that of an authentic sample of 1,5-anhydrocellobiitol. The disagreement between the observed melting point and the value reported in the literature is thought to be due to the existence of another crystalline form.

DIGLYCOLIC ACID DERIVATIVES OF GLUCOSIDES

D'-Methoxy-D-hydroxymethyl diglycolic acid was obtained as the strontium salt from Dr. J. W. Green. The corresponding C6 acid (D'-methoxy-D-carboxymethyl diglycolic acid) and L'-methoxy-D-hydroxymethyl diglycolic acid were prepared from methyl α-D-glucuronoside and methyl β-D-glucoside by Dr. N. S. Thompson. The periodic acid/bromine-water oxidation procedure of Jackson and Hudson (69) was used.

INTERNAL STANDARDS

Methyl α-D-mannopyranoside, ethyl 3,4,6-tri-O-methyl β-D-glucopyanoside, methyl tetra-O-methyl β-D-glucopyranoside, and cyclohexyl β-D-glucopyranoside were used as internal standards in the gas-liquid chromatographic analyses of reaction solutions. All were chromatographically pure as supplied from various sources.

WATER

All water used in preparing solutions, in analytical work, and in cleaning reactors was first deionized, then twice distilled. The second distillation was from alkaline permanganate (70) in an apparatus fitted with baffles and several bends in the distilling head to prevent spray entrainment.

SODIUM HYDROXIDE

A saturated solution of sodium hydroxide was prepared from reagent-grade pellets and freshly redistilled water. The solution was stored under a nitrogen atmosphere for several weeks to allow the sodium carbonate to precipitate. The supernatant solution was used to prepare 1.25N solution by dilution with carbon dioxide-free, doubly-distilled water. Solutions were stored under nitrogen atmospheres.

OXYGEN

Matheson Extra Dry Grade* oxygen was used. The purity is quoted in their catalog as 99.6% minimum. The dew point is quoted as below -70°F.

*The Matheson Company, P. O. Box 960, Joliet, Illinois.

APPENDIX III

EXPERIMENTAL METHODS

CLEANING REACTORS

Before being used for the first time, the reactors were cleaned by filling them with 5% sodium hydroxide solution, pressurizing with oxygen and heating at 120°C. in the oil bath for several hours. Subsequent cleaning and drying of the reactors was the same as after each reaction run.

With the valves removed, the reactors were rinsed at least four times with about 150 ml. of redistilled water each time. The last rinse was followed by a rinse with absolute ethanol (about 30 ml.) which aided in drying the reactor. The insides of the reactors were dried by inserting an aspirator probe to the sealed end of the inverted reaction chamber, and allowing the aspirator to pull air over the wet surfaces.

FILLING REACTORS

Each reactor with its valve removed was purged with oxygen by means of a probe connected to the oxygen source and extending to the bottom of the reactor. After purging, thirty milliliters of reaction solution were pipetted into the reactor, and the valve was replaced. The oxygen supply was connected to the end of the valve stem with a tire valve chuck, and the reactor was pressurized. The valve was sealed while the system was still under pressure. The oxygen supply was disconnected, and the valve cover was replaced. The reactor was placed in the hot oil bath.

OPENING REACTORS

After the desired reaction time, the reactors were cooled in a cold water bath and wiped clean externally. The pressure in each reactor was checked by connecting a gage to the end of the valve stem and opening the valve. The pressure was released slowly, and the valve was removed. Then, the reaction solution was poured into a glass bottle, which was subsequently sealed with a screw cap fitted with a polyethylene insert.

ANALYTICAL PROCEDURES

ANALYSIS OF UNREACTED GLUCOSIDE

The concentration of unreacted glucoside in a reaction solution was determined by gas chromatography. An aliquot (usually 1 ml.) of solution was combined with a known amount of internal standard in solution. Best results were obtained when the molar concentration of the internal standard solution was about 85% of that of the original glucoside concentration in the reaction solution. The mixed solution was treated in the following way for all reactants except methyl tetra-O-methyl β-D-glucoside and methyl 3,4,6-tri-O-methyl β-D-glucoside.

The solution was deionized by passing it through a small ion exchange column containing 2 ml. of Amberlite IR-120 (H^+) resin over 1 ml. of Amberlite MB-3 (mixed bed) resin. The column was washed with about 13 ml. of water in 5 or 6 portions, and the deionized solution and washings were concentrated together to dryness at 40-50 °C. under reduced pressure.

Trimethylsilyl ether (TMS) derivatives were prepared by adding TRI-SIL* to the dried material contained in 25-ml. Erlenmeyer flasks. The flasks were sealed with polyethylene stoppers and heated at about 70°C. for at least ten minutes with occasional shaking. The samples were cooled, after which the pyridine was removed on a rotary evaporator. An atmosphere of hexane was maintained in the evaporation system to prevent moisture from entering the flasks. Finally, the TMS derivatives were dissolved in hexane (0.3 ml. for each 4 mg. or less of material), and analyzed by gas chromatography. The conditions varied with the glucoside as shown in Table VIII.

Methyl 3,4,6-tri-O-methyl β-D-glucoside and methyl tetra-O-methyl β-D-glucoside were sufficiently volatile for gas chromatographic analysis and did not require derivative formation. Reaction solutions were mixed with internal standards and diluted to a known volume; then injected directly into the chromatograph. Conditions are shown in Table VIII.

Chromatogram peak areas were measured with a Disc Integrator and corrected manually for base-line shifts. The average area ratio of glucoside peak to internal standard peak was calculated from triplicate chromatograms of each sample. The ratio thus obtained was used to calculate the glucoside concentration in the reaction sample according to Equation (29).

*TRI-SIL is a commercial mixture of hexamethyl disilazane, trimethylchlorosilane and pyridine prepared by the Pierce Chemical Company, Rockford, Illinois. 0.6 Ml. were used for each 4 mg., or less, of material.

TABLE VIII

CHROMATOGRAPHIC CONDITIONS

Instrument – Varian/Aerograph Model 1200 with hydrogen flame ionization detector

Carrier gas – Nitrogen, 20 p.s.i.

Hydrogen – 8 p.s.i. (11 p.s.i. with Column B)

Injector temperature – 220°C. (285°C. with disaccharides)

Detector temperature – 220°C. (300°C. with disaccharides)

Column: A – 5' x 1/8" 5% SE-30 on Chrom W (DMCS) 60/80 mesh.

B – 5' x 1/8" 20% Butanediol succinate and Apiezon M on Chrom W 60/80 mesh.

Internal standards:

1 – Methyl α-D-mannopyranoside
2 – Ethyl 3,4,6-tri-O-methyl β-D-glucopyranoside
3 – Methyl tetra-O-methyl β-D-glucopyranoside
4 – Cyclohexyl β-D-glucopyranoside

Compound	Internal Standard	Column	Column Temp., °C.
Methyl β-D-glucoside	1	A	185
-2-deoxy	1	A	170
-6-deoxy	1	A	170
-tetra-O-methyl	2	B	190
-3,4,6-tri-O-methyl	3	B	190
-3-O-methyl (α,β)	1	A	165
Methyl β-D-xyloside	1	A	170
Cellobiitol	4	A	210 → 270 at 8°/min.
1,5-Anhydrocellobiitol	4	A	210 → 270 at 8°/min.

$$C = A \times F \times V_{is} \times C_{is}/V \qquad (29)$$

where

$\underline{C}$ = Concentration of glucoside.

$\underline{A}$ = Average area ratio of glucoside peak to internal standard peak.

$\underline{F}$ = Molar response factor (see below).

$\underline{V}_{\underline{is}}$ = Volume of internal standard solution used.

$\underline{C}_{\underline{is}}$ = Concentration of internal standard solution.

$\underline{V}$ = Volume of reaction sample aliquot.

Molar response factors ($\underline{F}$), defined by Equation (30), were determined by treating samples containing known molar ratios of glucoside and internal standard in the same manner as the reaction samples were treated.

$$F = ([G]/[IS])/(A_G/A_{is}) \qquad (30)$$

where

$[\underline{G}]/[\underline{IS}]$ = Molar ratio of glucoside to internal standard.

$\underline{A}_{\underline{G}}/\underline{A}_{\underline{is}}$ = Peak area ratio of glucoside to internal standard.

Response factors were found to be independent of the molar ratios in the range encountered in analysis. The average values are given in Table IX. Mean error was less than $\pm$ 1.5% in all cases.

TABLE IX

RESPONSE FACTORS

Compound	Internal Standard	Response Factor
Methyl β-D-glucoside	Methyl α-D-mannoside	1.02
-2 deoxy	Methyl α-D-mannoside	1.20
-6 deoxy	Methyl α-D-mannoside	1.19
-3-O-methyl (α,β)	Methyl α-D-mannoside	1.25
-tetra-O-methyl	Ethyl 3,4,6-tri-O-methyl β-D-glucoside	0.89
-3,4,6-tri-O-methyl	Methyl tetra-O-methyl β-D-glucoside	1.16
Methyl β-D-xyloside	Methyl α-D-mannoside	1.26
1,5-Anhydrocellobiitol	Cyclohexyl β-D-glucoside	0.49

DETERMINATION OF METHANOL

An aliquot* of the solution to be analyzed was pipetted into a 50-ml. round-bottom flask and diluted to about 30 ml. A single boiling chip was added, and the flask was connected to the distillation apparatus (Fig. 20). The distillate was collected at the rate of about 0.5 ml./min. in a volumetric flask (usually 10-ml. size) partially submerged in an ice-water bath. After about 9 ml. had been collected, the volumetric flask was removed, warmed to room temperature and filled to the mark with redistilled water. The methanol content of the distillate was determined colorimetrically by a procedure adapted from the original chromotropic acid method of Boos (71). The method involves oxidizing the methanol to formaldehyde, complexing the formaldehyde with chromotropic acid and measuring the absorbance of the resulting magenta-colored solutions. The detailed procedure follows:

*The volume of the aliquot varied depending on the amount of methanol thought to be present.

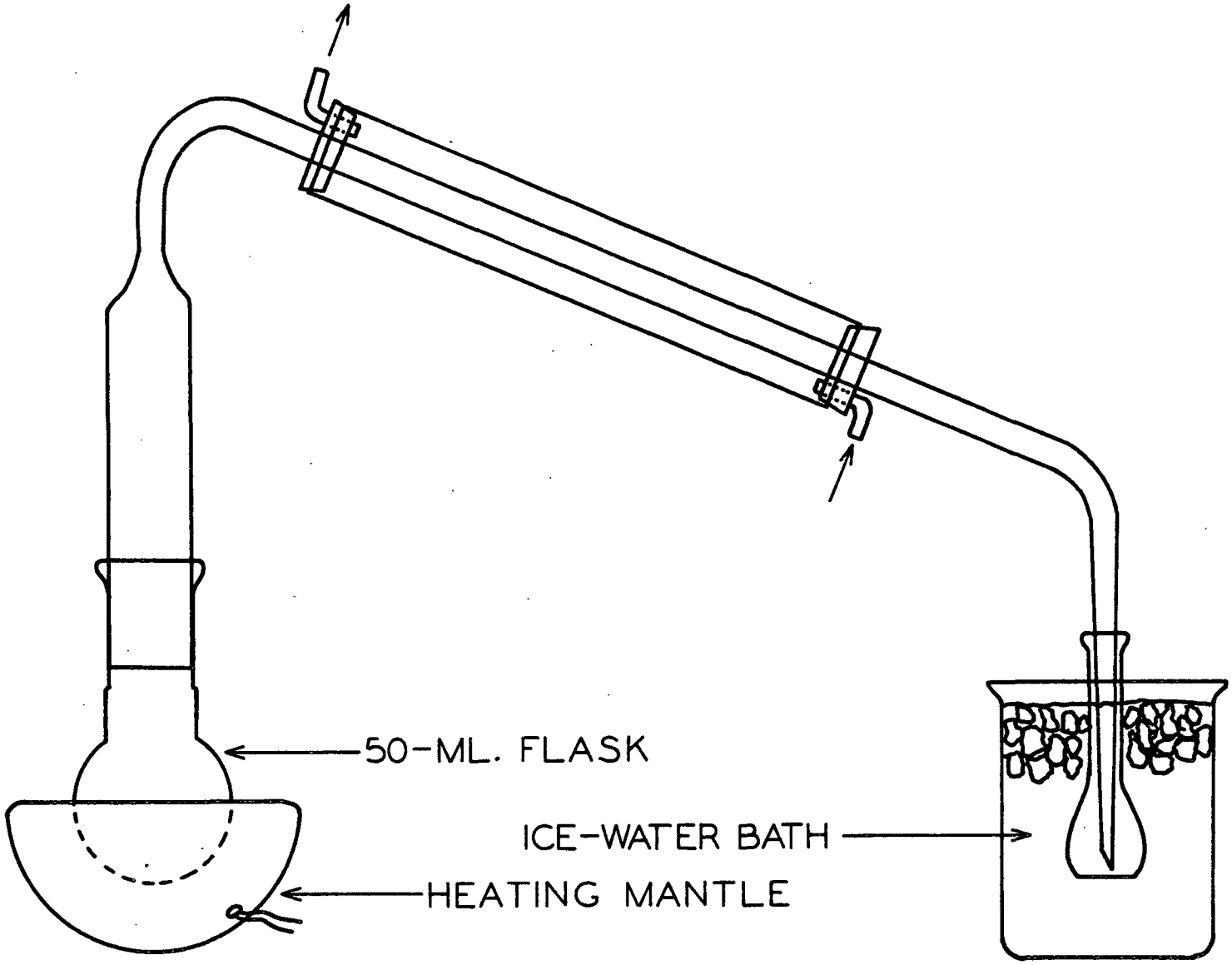


Figure 20. Methanol Distillation Apparatus (One-Half Actual Size)

1. To 1 ml. of test solution in a 10-ml. volumetric flask in an ice-water bath add 5 drops of phosphoric acid.
2. Add 0.25 ml. of 6% $KMnO_4$ (MnO_2-free) from a 0.5 ml. Tuberculin syringe, and start timer.
3. Allow oxidation reaction to proceed at 0°C. for 6 min. from time of addition of $KMnO_4$. Stop reaction by the addition of 0.35 ml. of 10% $NaHSO_3$ from a Tuberculin syringe. Solution should be colorless.
4. With cooling, add 5 ml. of concentrated sulfuric acid. Allow mixture to cool to 0°C.; then mix by swirling.
5. Add 5 drops of 5% aqueous chromotropic acid (prepared from reagent-grade sodium salt).
6. Develop colored complex by heating in boiling-water bath for 15 min., with stoppers loosely in place.
7. Cool and dilute to near mark with doubly-distilled water. Mix by shaking.
8. Cool to room temperature and dilute to mark. Mix well by shaking.
9. Read absorbance of solution at 576 nm. against doubly-distilled water blank. A Beckman DU spectrophotometer was used in this work.
10. Correct absorbances for average absorbance of reagent blank.
11. Convert absorbance readings to concentration values through equation of calibration plot determined with samples of known methanol concentrations.

The calibration plot used in this work is shown with its 95% confidence limits in Fig. 21. The data were obtained on five different days using different batches of reagent solutions as well as different standard solutions of methanol. A least squares fit of the data gives a straight line which is best described by Equation (31) where $[\underline{M}]$ is the methanol concentration in mmoles/liter and $\underline{A}$ is the corrected absorbance.

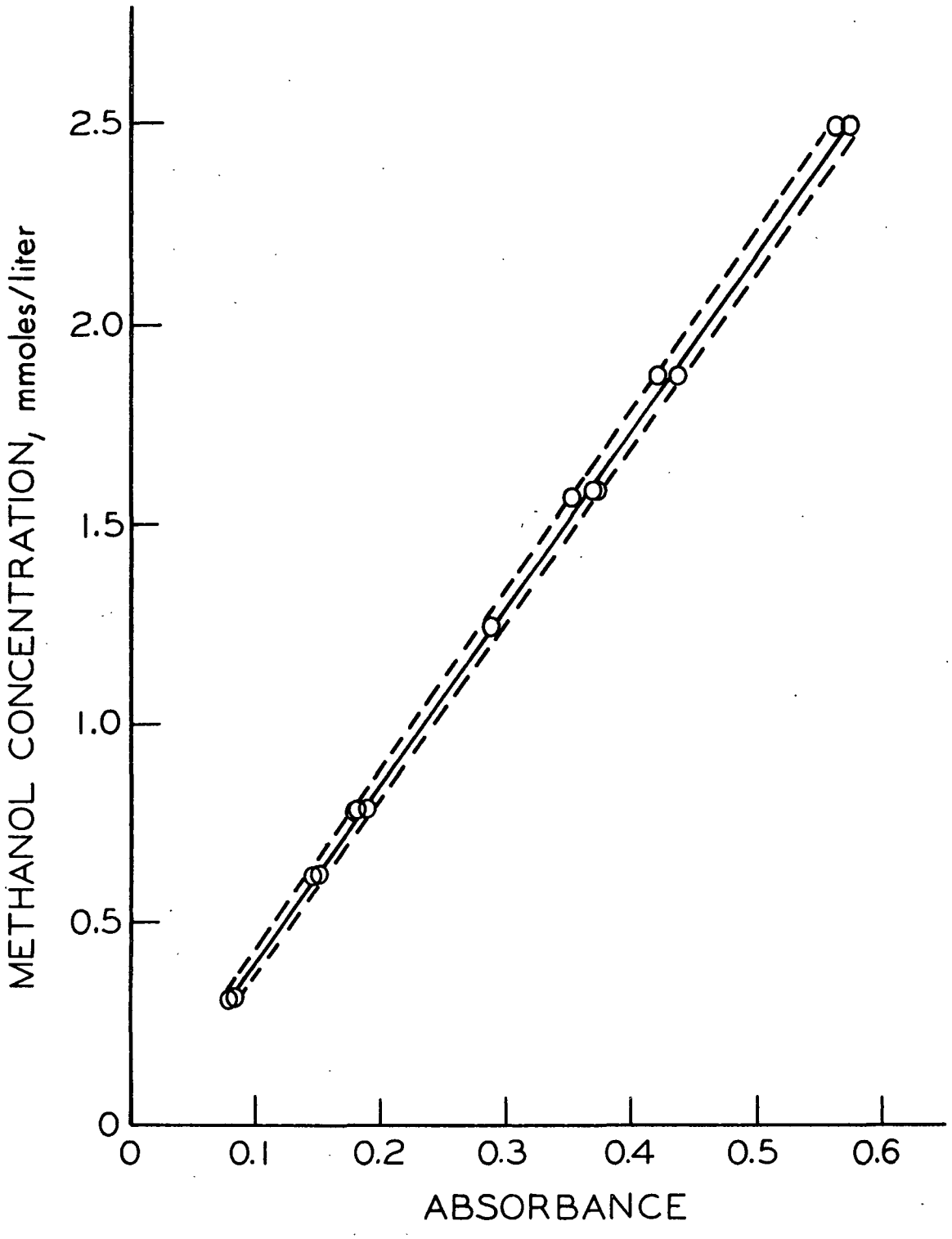


Figure 21. Methanol Calibration Plot

$$[M] = 4.479(A) - 0.044 \qquad (31).$$

The methanol concentrations in the reaction samples were calculated from Equation (32).

$$[M]_{RS} = (V_d/V_s)[4.479(A) - 0.044] \qquad (32)$$

where

$[\underline{M}]_{\underline{RS}}$ = Methanol concentration in reaction sample, mmoles/liter.

$\underline{V_d}$ = Volume of distillate after dilution (usually 10 ml.).

$\underline{V_s}$ = Volume of reaction sample taken for distillation.

$\underline{A}$ = Absorbance (corrected).

DETERMINATION OF PEROXIDES

Peroxides were determined by the following procedure adapted from the iodometric method described by Kolthoff and Sandell (72). Analysis was done within 15 min. after cooling reactors.

1. To 25 ml. of reaction solution in a 250-ml. Erlenmeyer flask add 20 ml. sulfuric acid (4N).
2. Add two portions (about 1/4 g. each) of sodium carbonate with gentle swirling after each addition. The carbon dioxide generated displaces the dissolved oxygen.
3. Add 3 drops of 3% ammonium molybdate solution.
4. Add 10 ml. of 10% KI solution.
5. Titrate with standard (0.01N) sodium thiosulfate.
6. Calculate peroxide concentration of sample (as H_2O_2) by Equation (33).

$$[\text{Peroxide}] = V_t\, C_t/(2\, V_s) \qquad (33)$$

where

$\underline{V}_t$ = Volume of sodium thiosulfate used,

$\underline{C}_t$ = Concentration of thiosulfate solution,

$\underline{V}_s$ = Volume of sample.

ACID HYDROLYSIS PROCEDURE

Bound methanol formed during the degradation of methyl β-D-glucoside was determined by subjecting the reaction solutions to acid hydrolysis and measuring the methanol produced.

Hydrolysis was done in an apparatus consisting of a 50-ml. round-bottom flask having a rubber stopper through which a short piece of glass tubing (9 mm. diam.) passed. A rubber septum sealed the outer end of the tubing.

The following procedure was used:

1. Evacuate the flask through a syringe needle inserted through the septum.
2. Inject sample to be hydrolyzed (5 ml., about 1.25N in NaOH).
3. Inject dilution water (10 ml.).
4. Inject HCl (10 ml., 6.63N) to neutralize NaOH in sample and provide excess acidity. Final solution will be about 2N in acid.
5. Heat in 80°C. bath for about 24 hours.
6. Cool to 0°C. and inject NaOH solution (5.5 ml., 12N) to make solution slightly alkaline.
7. Remove stopper and connect flask to methanol distillation apparatus (Fig. 20). Collect distillate in volumetric flask (25 ml.) and dilute as usual.
8. Determine methanol as usual.

METHOD USED IN INVESTIGATING ACIDIC REACTION PRODUCTS

Acidic reaction products were detected as trimethylsilyl ether and ester derivatives by gas-liquid chromatography. Reaction solutions were passed through ion-exchange columns containing Amberlite IR-120(H^+) resin. They were collected in flasks to which a small amount of sodium hydroxide had been added so that the final pH of the solution and washings would be about 9-10. This prevented lactone formation. The solutions were concentrated to dryness under reduced pressure at below 45°C. Derivatives were prepared as described in this Appendix for the analysis of glucoside. Gas chromatography was done with a 5' x 1/8" column of SE-30 (5%) on Chrom W (DMCS) 60/80 mesh at a column temperature of 170°C. and a carrier gas flow rate of 20 ml./min. (20 p.s.i. N_2). Peak retention times were compared to those of known samples (see Appendix VI).

APPENDIX IV

GAS CHROMATOGRAPHIC RETENTION TIMES OF SOME SELECTED SUGARS, GLYCOSIDES, ACIDS AND LACTONES

During the course of attempting to identify acidic reaction products, a number of known compounds were chromatographed as their trimethylsilyl (TMS) derivatives in order to establish a rough correlation between molecular structure and retention time. The retention times relative to methyl β-D-glucoside (TMS) are presented in Table X. The retention time of MBG-TMS is 15.0 minutes.

The following conditions were used in all cases.

Varian Model 1200 chromatograph with Hydrogen Flame Ionization Detector

Column: 5' x 1/8" – 5% SE-30 on 60/80 mesh Chromosorb W (DMCS).

Oven temperature – 170°C.

Injector temperature – 210°C.

Detector temperature – 210°C.

Nitrogen carrier gas – 20 p.s.i.

Hydrogen – 8 p.s.i.

TABLE X

GAS CHROMATOGRAPHIC RETENTION TIMES OF THE DERIVATIVES OF SELECTED COMPOUNDS

TMS Derivative of	Relative Retention Time (MBG-TMS = 1.00)
Sugars	
Arabinose	0.28
Levoglucosan	0.38
Xylose	0.42
2-Deoxy α-D-glucose	0.46
3-O-Methyl α-D-glucose	0.54
Glyceraldehyde	0.59
2-Deoxy β-D-glucose	0.62
Fructose	0.71
3-O-Methyl β-D-glucose	0.85
α-D-Glucose	0.99
β-D-Glucose	1.58
Glycosides	
Methyl β-D-arabinopyranoside	0.18
Methyl α-D-xylopyranoside	0.32
Methyl 2-deoxy α-D-glucopyranoside	0.34
Methyl β-D-xylopyranoside	0.35
Methyl 2-deoxy β-D-glucopyranoside	0.41
Methyl 6-deoxy β-D-glucopyranoside	0.44
Methyl 3-O-methyl α-D-glucopyranoside	0.46
Methyl 3-O-methyl β-D-glucopyranoside	0.46

TABLE X (Continued)

GAS CHROMATOGRAPHIC RETENTION TIMES OF TMS DERIVATIVES OF SELECTED COMPOUNDS

TMS Derivative of	Relative Retention Time (MBG-TMS = 1.00)
Glycosides (Contd)	
Methyl α-D-mannopyranoside	0.63
Methyl β-D-glucopyranoside	1.00
Methyl β-D-glucuronopyranoside	1.24
Isopropyl β-D-glucopyranoside	1.32
Acids and Lactones	
Oxalic acid	0.02
Glyceric acid	0.10
Erythronic acid	0.21
Tartaric acid	0.29
α-D-Glucoisosaccharinic lactone	0.35
D'-Methoxy-D-hydroxymethyl diglycolic acid[a]	0.40
L'-Methoxy-D-hydroxymethyl diglycolic acid[b]	0.43
α-D-Glucoisosaccharinic acid	0.51
Xylonic acid	0.55
D'-Methoxy-D-carboxymethyl diglycolic acid[c]	0.59
Arabinonic acid	0.62
D-Glucuronolactone	0.64
α-Metasaccharinic acid	0.86
β-Metasaccharinic acid	0.87
2-Ketogluconic acid	0.87

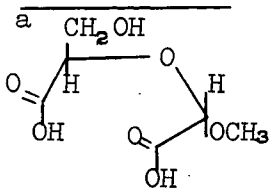
See end of table for footnotes.

TABLE X (Continued)

GAS CHROMATOGRAPHIC RETENTION TIMES OF TMS DERIVATIVES OF SELECTED COMPOUNDS

TMS Derivative of	Relative Retention Time (MBG-TMS = 1.00)
Acids and Lactones (Contd)	
D-Gluconic lactone	0.87
5-Ketogluconic lactone	1.00
5-Ketogluconic acid	1.16
Methyl β-D-glucuronopyranoside	1.24
Saccharic acid	1.64
D-Gluconic acid	1.68
D-Glucuronic acid	1.92

a



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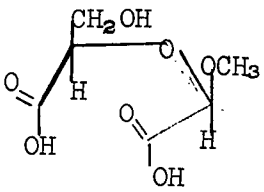

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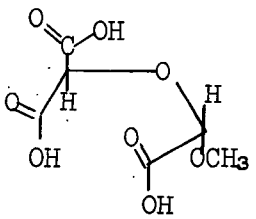

APPENDIX V

SOLUBILITY OF OXYGEN IN SODIUM HYDROXIDE SOLUTION

The relationship between oxygen solubility, oxygen pressure and sodium hydroxide concentration at 120°C. was estimated by linear interpolation of Bruhn's data (34) shown in Table XI.

TABLE XI

SOLUBILITY OF OXYGEN IN SODIUM HYDROXIDE SOLUTIONS AT 100 AND 150°C. (34)

Temp., °C.	NaOH, N	α[a]
100	0.5	0.0160
	1.0	0.01225
	1.5	0.01052
150	0.5	0.01692
	1.0	0.01356
	1.5	0.01104

[a] α = Solubility of oxygen in $cm.^3$ at standard conditions per ml. of solution per atmosphere of oxygen.

Values of α corresponding to sodium hydroxide concentrations of 0.5, 0.875 and 1.25N and a temperature of 120°C. were obtained by interpolation of the data in Table X. Oxygen pressures required for each level of alkali to give dissolved oxygen concentrations equivalent to that in a 1.25N NaOH solution at 120°C. and 74.5 p.s.i.a. oxygen (measured at 25°C.) were then calculated by Equation (34). The results are given in Table XII.

$$p_{O_2} = [O_2]_s/\alpha \qquad (34)$$

where p_{O_2} = oxygen pressure required

$[O_2]_s$ = dissolved oxygen in 1.25N NaOH at 120°C. and 74.5 p.s.i. $O_2 = \alpha_{120°C.,\ 1.25N} \times (74.5/14.7)$

α = solubility coefficient for given NaOH concentration.

TABLE XII

ESTIMATED SOLUBILITIES OF OXYGEN IN SODIUM HYDROXIDE SOLUTIONS AT 120°C.

NaOH, N	α	p_{O_2}, p.s.i.a. at 25°C.	$O_2 \times 10^3$ mmoles/g. H_2O
0.50	0.01461	54.5	1.83
0.875	0.01273	63.7	1.87
1.25	0.01100	74.5	1.89

APPENDIX VI

KINETIC DATA

The data on the unreacted glucoside and methanol produced during the kinetic runs are presented in the following tables. Also included, for those runs in which methanol was determined, are the ratios of methanol found to the theoretically possible yield of methanol from glycosidic bond cleavage. For small extents of reaction the calculated value of this ratio may be subject to considerable error because its calculation involves a difference in numbers which is small compared to the analytical errors.

TABLE XIII

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

Time, hr.	Unreacted MBG Concn., $\underline{M} \times 10^3$	Methanol Concn., $\underline{M} \times 10^3$	$\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$
$[MBG]_o = 0.01001\underline{M}$; $[NaOH] = 1.25\underline{N}$; $\underline{p}_{O_2} = 43$ p.s.i.a.; $\underline{T} = 120°C$.			
0	10.00	0.000	--
6.0	9.25	0.304	0.405
11.0	9.00	0.471	0.471
16.5	8.60	0.748	0.534
24.0	8.27	0.966	0.558
36.5	7.75	1.065	0.473
48.0	7.01	1.466	0.490
62.0	6.49	2.089	0.595
84.0	6.05	2.302	0.584

TABLE XIII (Continued)

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

Time, hr.	Unreacted MBG Concn., $\underline{M} \times 10^3$	Methanol Concn., $\underline{M} \times 10^3$	$\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$
$[MBG]_o = 0.01046\underline{M}$; [NaOH] = 1.25$\underline{N}$; $\underline{p}_{O_2}$ = 74.5 p.s.i.a.; $\underline{T}$ = 120°C.			
0	10.48	0.000	--
2.0	10.29	0.164	0.965
4.0	10.19	0.285	1.056
8.0	9.41	0.573	0.546
12.0	9.31	0.712	0.619
16.0	8.47	1.089	0.547
20.0	8.27	1.233	0.563
28.0	7.83	1.433	0.545
32.0	7.11	1.793	0.535
$[MBG]_o = 0.01000\underline{M}$; [NaOH] = 1.25$\underline{N}$; $\underline{p}_{O_2}$ = 74.5 p.s.i.a.; $\underline{T}$ = 120°C.			
0	9.95	0.000	--
5.0	9.39	0.402	0.659
10.0	9.13	0.690	0.793
15.1	8.56	0.904	0.628
20.0	8.11	1.227	0.649
30.0	7.48	1.600	0.635
$[MBG]_o = 0.02902\underline{M}$; [NaOH] = 1.25$\underline{N}$; $\underline{p}_{O_2}$ = 74.5 p.s.i.a.; $\underline{T}$ = 120°C.			
0	29.63	--	--
2.0	28.09	--	--
4.0	26.14	--	--
8.0	24.47	--	--
11.5	23.25	--	--
$[MBG]_o = 0.01046\underline{M}$; [NaOH] = 1.25$\underline{N}$; $\underline{p}_{O_2}$ = 0, Nitrogen; $\underline{T}$ = 120°C.			
0	10.48	0.00	--
16.0	10.78	0.047	--
31.5	10.38	0.118	--
$[MBG]_o = 0.009976\underline{M}$; [NaOH] = 1.25$\underline{N}$; $\underline{p}_{O_2}$ = 54.5 p.s.i.a.; $\underline{T}$ = 120°C.			
0	9.90	0.000	--
5.3	9.53	0.282	0.632
10.0	9.15	0.543	0.657
19.9	8.57	0.578	0.411
30.0	8.00	1.260	0.638
40.4	7.50	1.536	0.620

TABLE XIII (Continued)

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

Time, hr.	Unreacted MBG Concn., M x 10^3	Methanol Concn., M x 10^3	$\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$
$[MBG]_o$ = 0.01000M; [NaOH] = 1.25N; p_{O_2} = 34.5 p.s.i.a.; T = 120°C.			
0	9.95	0.000	--
5.3	9.54	0.237	0.515
5.5	9.46	--	--
10.0	9.32	0.406	0.597
10.0	9.22	--	--
15.0	--	0.538	--
20.8	8.94	0.786	0.742
30.3	8.65	0.989	0.733
40.0	8.36	1.187	0.724
50.0	7.92	1.399	0.673
$[MBG]_o$ = 0.01001M; [NaOH] = 0.875N; p_{O_2} = 63.7 p.s.i.a.; T = 120°C.			
0	10.22	0.000	--
5.0	9.95	0.200	3.333
10.0	9.64	0.366	0.989
20.0	9.17	0.691	0.823
28.5	8.80	0.833	0.688
40.1	8.50	1.085	0.718
50.5	8.13	1.368	0.728
Same Conditions Except Hydroquinone Added $[\text{Hydroquinone}]_o$ = 0.208 g./l.			
12.0	8.51	1.179	0.786
24.0	7.27	1.753	0.640
$[MBG]_o$ = 0.009989M; [NaOH] = 0.500N; p_{O_2} = 54.5 p.s.i.a.; T = 120°C.			
0	10.12	0.000	--
10.2	9.67	0.179	0.561
20.1	9.42	0.293	0.515
30.0	9.21	0.433	0.556
40.5	8.91	0.604	0.560
51.8	8.83	0.769	0.664
$[MBG]_o$ = 0.01001M; [NaOH] = 1.25N; p_{O_2} = 74.5 p.s.i.a.; T = 110°C.			
0	10.13	0.000	--
12.0	9.42	0.379	0.642
24.1	8.87	0.748	0.656
37.6	8.50	0.992	0.657
48.1	7.87	1.228	0.574
60.0	7.82	1.347	0.615
72.8	7.11	1.742	0.601

TABLE XIII (Continued)

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

Time, hr.	Unreacted MBG Concn., $\underline{M} \times 10^3$	Methanol Concn., $\underline{M} \times 10^3$	$\frac{[\text{Methanol}]}{[\text{Methanol}]_{\text{theor.}}}$
$[MBG]_o = 0.01000\underline{M}$; $[NaOH] = 1.25\underline{N}$; $\underline{p}_{O_2} = 74.5$ p.s.i.a.; $\underline{T} = 99°C.$			
0	10.20	0.000	--
23.0	9.67	0.277	0.839
46.0	9.11	0.534	0.600
70.0	8.70	0.699	0.538
93.2	8.36	0.873	0.532
117.0	7.94	1.073	0.521
142.0	7.68	1.306	0.563

TABLE XIV

DEGRADATION OF METHYL TETRA-O-METHYL β-D-GLUCOPYRANOSIDE

$[MTMBG]_o = 0.01001\underline{M}$; $[NaOH] = 1.25\underline{N}$; $\underline{p}_{O_2} = 74.5$ p.s.i.a.; $\underline{T} = 120°C.$

Time, hr.	Unreacted MTMBG Concn., $\underline{M} \times 10^3$
0	10.00
4.0	10.03
15.0	10.09
45.0	9.97
51.0	9.97

TABLE XV

DEGRADATION OF METHYL 3,4,6-TRI-O-METHYL β-D-GLUCOPYRANOSIDE

$[M3,4,6TMBG]_o$ = 0.01000M; [NaOH] = 1.25N; p_{O_2} = 74.5 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted M3,4,6TMBG Concn., M x 10^3	Methanol Concn., M x 10^3
0	10.00	0.000
7.8	9.53	0.195
15.0	9.75	0.355
20.0	9.49	0.406
39.7	9.77	0.751
50.0	9.38	0.721

TABLE XVI

DEGRADATION OF METHYL 2-DEOXY-β-D-GLUCOPYRANOSIDE

$[M2DBG]_o$ = 0.009992M; [NaOH] = 1.25N; p_{O_2} = 74.5 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted M2DBG Concn., M x 10^3	Methanol Concn., M x 10^3	$\frac{[Methanol]}{[Methanol]_{theor.}}$
0	10.01	0.000	--
9.5	8.54	1.717	1.182
16.0	7.89	2.392	1.138
24.0	7.39	2.862	1.101
32.0	6.64	3.660	1.092
40.0	5.98	4.201	1.047

$[M2DMBG]_o$ = 0.01000M; [NaOH] = 1.25N; p_{O_2} = 0, Nitrogen; T = 120°C.

0	10.00	--	--
11.0	10.15	--	--
24.0	9.78	--	--
36.3	9.92	--	--
48.0	9.88	--	--

TABLE XVII

DEGRADATION OF METHYL 6-DEOXY-β-D-GLUCOPYRANOSIDE

$[M6DBG]_o$ = 0.01001M; [NaOH] = 1.25N; p_{O_2} = 7.45 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted M6DBG Concn., M x 10^3	Methanol Concn., M x 10^3	$\frac{[Methanol]}{[Methanol]_{theor.}}$
0	9.96	0.000	--
5.0	9.84	0.176	1.03
9.5	9.62	0.311	0.797
20.0	9.07	0.649	0.690
30.1	8.40	0.941	0.478
50.4	7.76	1.122	0.499

TABLE XVIII

DEGRADATION OF METHYL β-D-XYLOPYRANOSIDE

$[MBX]_o$ = 0.009995M; [NaOH] = 1.25N; p_{O_2} = 74.5 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted MBX Concn., M x 10^3	Methanol Concn., M x 10^3	$\frac{[Methanol]}{[Methanol]_{theor.}}$
0	9.89	0.000	--
5.0	9.51	0.124	0.256
11.0	8.96	0.471	0.455
20.0	8.56	0.600	0.418
29.8	8.09	0.934	0.490
40.6	7.61	1.099	0.461
50.2	7.21	1.488	0.534

TABLE XIX

DEGRADATION OF METHYL 3-O-METHYL (α,β)-D-GLUCOPYRANOSIDE

$[M3MG] = 0.009769\underline{M}$ (approximately 47% β-anomer)

$[NaOH]_o = 1.25$; $\underline{p}_{O_2} = 74.5$ p.s.i.a.; $\underline{T} = 120°C.$

Time, hr.	Unreacted M3MG Concn., $\underline{M} \times 10^3$
0	10.00
11.5	9.50
24.0	9.17
48.0	8.04

TABLE XX

DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE
IN THE PRESENCE OF GLUCOSE

$[MBG]_o = 0.01001\underline{M}$; $[NaOH] = 1.25\underline{N}$; $\underline{p}_{O_2} = 74.5$ p.s.i.a.; $\underline{T} = 120°C.$

$[Glucose]_o = 0.00015\underline{M}$

Time, hr.	Unreacted MBG Concn., $\underline{M} \times 10^3$	Methanol Concn., $\underline{M} \times 10^3$	$\frac{[Methanol]}{[Methanol]_{theor.}}$
0	10.00	0.000	--
2.0	9.61	0.289	0.723
4.0	9.22	0.466	0.590
8.0	8.64	0.774	0.565
14.0	8.11	0.991	0.522
23.0	7.91	1.196	0.570

TABLE XXI

EFFECT OF METALS ON DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

$[MBG]_o$ = 0.01M; [NaOH] = 1.25N; p_{O_2} = 43 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted MBG Concn., M x 10^3	
	Teflon-Lined Reactor	Stainless[a] Steel Reactor
0.0	10.00	10.00
12.3	8.87	7.93
23.6	8.56	6.98
47.5	7.52	6.40

[a] Type 316.

TABLE XXII

EFFECT OF MAGNESIUM CARBONATE ON DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE

$[MBG]_o$ = 0.01M; [NaOH] = 1.25N; p_{O_2} = 74.5 p.s.i.a.; T = 120°C.

Time, hr.	Unreacted MBG Concn., M x 10^3
0.0	10.22
21.4	8.60
44.0	7.55

APPENDIX VII

PROPOSED DESIGN FOR TEFLON-LINED REACTOR THAT CAN BE SAMPLED DURING REACTION

A reactor lined with teflon (or another inert material) and capable of being sampled while hot and under pressure would be a great aid to future model studies of oxygen bleaching reactions. Such a reactor would have a number of advantages over the tube-type reactors used in this thesis. Degradation of models could be studied more conveniently, but sampling a volatile product, e.g., methanol, would still be easier in the tube-type reactor.

Designs of a new type of reactor were considered. The one presented and discussed here comprises an easily constructed, completely teflon-lined, stainless steel system with considerable versatility, and utilizes commercially available components wherever possible. Dimensions can be varied to suit particular conditions of solution volume, sample size, etc. The basic reactor assembly is sketched in Fig. 22. A schematic of the system with accessories for filling and sampling is shown in Fig. 23.

GENERAL DESCRIPTION

The basic design consists of a stainless steel pot lined with a machined, teflon insert. The cover is coated with a cast film of teflon or Kel-F and is bolted to the pot by means of flange fittings. The contact of the cover plate and the upper edge of the teflon insert provides the main seal. An "O" ring can be used for a secondary seal.

Sampling and introduction of reaction solution if desired, is done through teflon spaghetti tubing as shown in Fig. 22. The tubing is reinforced with a

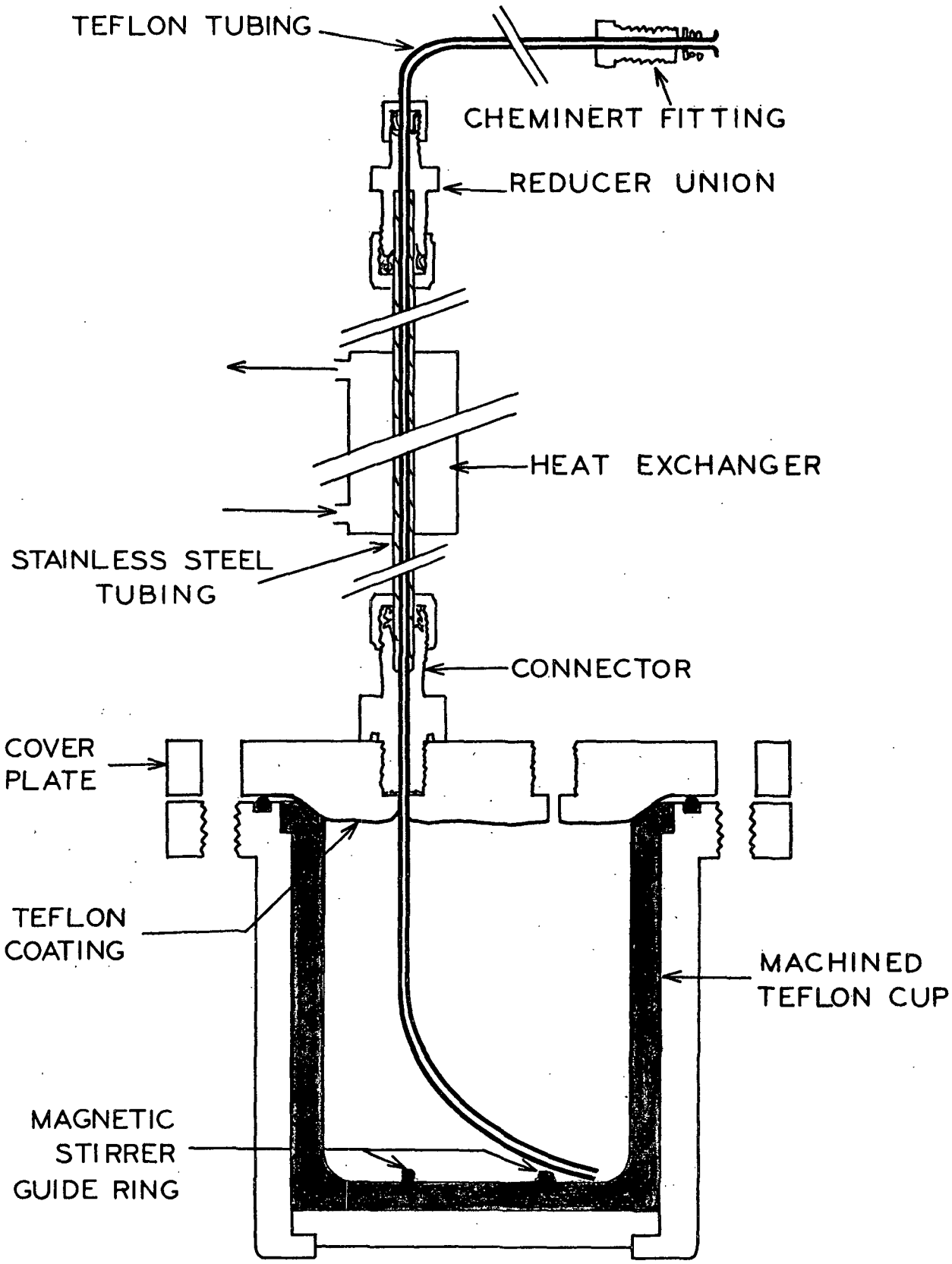

Figure 22. Proposed Design for Lined Reactor and Sampling Apparatus

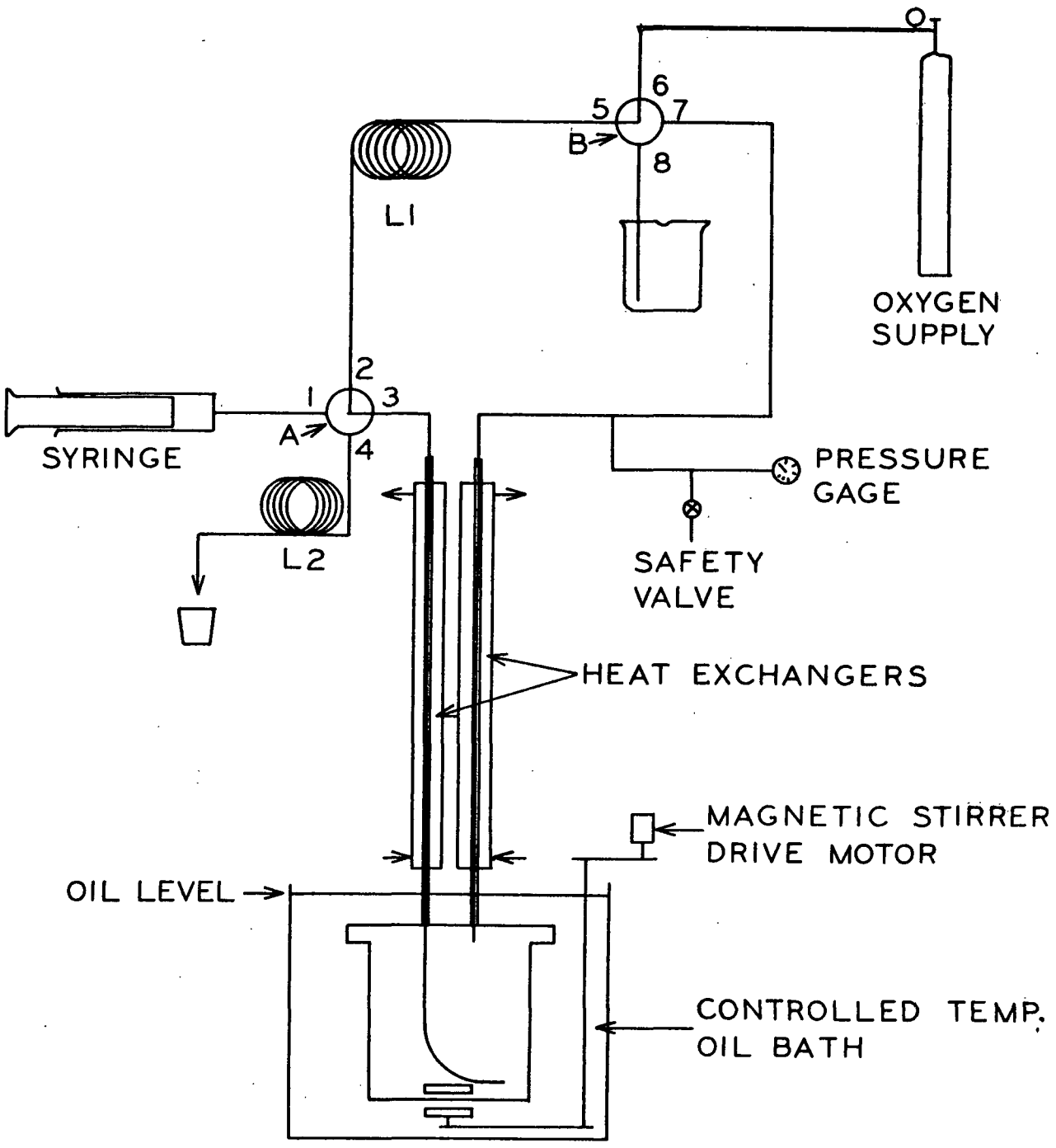

Figure 23. Schematic of Reactor and Fitting Connections

tightly fitting sheath of stainless steel tubing throughout its heated portion. It is cooled by a heat exchanger surrounding the stainless steel tubing above the oil bath. When the teflon tubing is cooled to near room temperature it will withstand pressures to about 500 p.s.i. without reinforcement.

Seals to prevent gas leaks around the teflon tubing are provided by compression fittings and a snug fit between the tubing and the coating on the inside of the cover plate. An additional seal could be incorporated by beveling the bottom edge of the hole through the connector and using a ferrule. The cover plate would provide the backing for the ferrule.

The same principle can be used for other ports to allow for gas sampling, temperature or pressure measurement, and, with a suitable pump, recirculation of the oxygen through the solution.

Figure 23 shows a sketch of a reactor with two ports and related tubing and valves which will allow for introduction of reaction solution into the reactor, sampling of solution and gas phases, back flushing of sampling lines, and cleaning of sample loops. To illustrate these operations consider the following examples:

1. Introduce alkaline solution into reactor, pressurize, seal and heat to temperature in oil bath.
2. Fill loop L1 with reactant solution in beaker by withdrawing plunger of syringe while Ports 5 and 8 of Valve B and Ports 1 and 4 of Valve A are connected.
3. Connect Ports 2 and 3 of Valve A and 5 and 6 of Valve B and force sample in Loop L1 into reactor.

4. With valves adjusted as in Step 2, Loop L1 can be flushed with water and dried.
5. Sample reactor by filling Loop L2 with Ports 3 and 4 open; then force solution out of loop by connecting Ports 1 and 4 and applying pressure with syringe.
6. The tubing from reactor to Valve A can be back flushed by applying oxygen pressure through Valve B(5-6), L1 and Valve A(2-3).
7. Gas phase samples can be taken by through Valve B(7-8).
8. Sample Loop L2 can be flushed and cleaned with syringe and Valve A open at 1 and 4.

SUGGESTED MATERIALS

Use 316 stainless steel for all metal parts.

1. Tubing

   Teflon – 0.063" O.D. x 0.031" I.D. (or 0.023" I.D.)

   Stainless steel – seamless 0.125" O.D. x 0.069" I.D. (less than Rockwell Hardness B90).

2. Heat Exchange – custom made or fashioned from tubing and Gyrolok[1] Heat Exchange Tees XT.
3. Connector (Fig. 22) – Gyrolok[1] No. 2COS-316.
4. Reducer Union (Fig. 22) – Gyrolok[1] No. 2RU1-316.
5. Cool-line fittings – Chromatronix[2] standard fittings.

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[1] Hoke Mfg. Co., Box 501, Tenafly, N. J., 07670.

[2] Chromatronix, Inc., 2743 Ninth Street, Berkeley, California, 94710.

COMMENTS

It may be necessary to shrink the teflon tubing slightly in the radial direction to get it to slip inside the stainless steel tubing. This can be done by pulling it through a series of holes in the manner used to get the sleeves into the tube-type reactors (see Appendix I).

Because of the creep tendency of conventional polytetrafluoroethylene (PTFE), pressure will deform the teflon. Consequently, with continued use, it may become increasingly difficult to seal the reactor at the cover joint. The problem can often be remedied by taking advantage of the excellent memory of the polymer. Upon heating to near its crystalline melting point, it will recover to its predeformed configuration. A more permanent solution to the problem would be to use a creep-resistant polymer. A new creep-resistant PTFE polymer, Halon G-700*, has been developed, and promises to greatly reduce the cold flow problem of conventional PTFE (73).

*Allied Chemical Corp., Plastics Div., P. O. Box 365, Morristown, N. J., 07960.